Scattering of light by light in crystals

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The probability of the effect is found for a molecular crystal and, in contrast to a previous publication on this topic [V. L. Strizhevskiĭ and V. V. Obukhovskiĭ, Sov. Phys. JETP **31**, 500 (1970)], allowance is made for anharmonism in the Coulomb subsystem and for the kinematic interaction between the excitons. It is shown that the contribution of these factors is not small in comparison with the factors taken into account by Strizhevskiĭ and Obukhovskiĭ. It can be isolated by measurements of the scattered intensity as a function of frequency and polarization. It is shown that the excitation spectrum should contain a peak whose position can be used to determine the bound-state energy.

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INTRODUCTION

Elementary light-by-light scattering (LLS) constitutes the disappearance of two photons of frequency ω_1 and ω_2 and the appearance of two other photons of frequency ω_3 and ω_4. The cross section for this effect in vacuum is 10^{-33} cm^2, which lies outside the range of modern experiments (see, for example, Ref. 1). However, in condensed media, the interaction between the electromagnetic field and the charges of particles that are the constituents of the medium ensures that the cross section is $\sigma \sim 10^{-28}$ cm^2, which *can* be detected with modern equipment.

As far as we know, the first publication[2] on the observation of LLS was concerned with the study of this effect in a CdS crystal for which radiation was observed at the frequency $\omega_4 = \omega_1 + \omega_2 - \omega_3$, where $\omega_3 \leqslant \omega_1 + \omega_2$, $\omega_1 \sim \omega_2$, and the intensity of this radiation was a rapidly-varying function of the scattering angle. This variation was used as a basis for the conclusion that it was LLS and not some other effect that was observed. Similar experiments were subsequently described in a number of publications, in which the specimens were calcite crystals[3] and water.[4] Measurements of LLS in gases of different density have also been reported.[5] It is clear that the LLS intensity in a gas is lower as compared with a condensed medium because of the lower density of scattering particles (atoms or molecules). The effect can then be enhanced by ensuring that the frequency of the primary radiation is close to the electron transition frequency. This idea was implemented in Ref. 6, where potassium vapor was used as the scattering medium.

The situation where $\hbar(\omega_1 + \omega_2)$ lies in the neighborhood of the energy of diexciton states was investigated in Ref. 7, where a study was reported of small-angle hyper-Raman scattering under conditions where it was essentially identical with LLS. The scattered intensity is then found to increase as $\omega_1 + \omega_2$ approaches the band of bound states, and it was shown that this effect could be exploited to investigate the polariton spectrum.

The first theoretical paper devoted to LLS appears to be Ref. 8, in which the probability of the effect and the scattered intensity were determined. The zero-order Hamiltonian in Ref. 8 describes the behavior of photons and electrons that do not interact with one another, and the perturbation is provided by the operator for the interactions between the photons and the electrons. The author of this paper also notes the possible interpretation of LLS as two successive three-photon processes, and shows that the intensity of this type of cascade process exceeds the LLS intensity by a factor of about 100. We note, however, that a suitable choice of the geometry of the experiment will exclude the contribution due to cascade processes because these two effects obey different laws of wave-vector conservation (phase matching conditions).

Another feature of LLS is that the differential LLS intensity per unit spectral and angular intervals is a quadratic function of the scattering volume.[9] The integrated power of the scattered radiation, on the other hand, is determined by the simple noncoherent sum of contributions due to all points within the scattering volume.

The spectral shape of LLS was investigated in Refs. 9 and 10. It depends on the absorption coefficient for the scattered and primary waves and on the spectral and amplitude distributions of the latter.

A more detailed and complete description of LLS can be achieved once an expression for the scattering probability is obtained within the framework of a microtheory. Such a theory was put forward in Ref. 11, in which the LLS tensor was evaluated explicitly for a model of a molecular crystal. The polaritons were treated as quasiparticles describing the propagation of radiation in the crystal, and it was shown that, when one of the polaritons appearing during the LLS process lies on the lower branch, it enters the exciton part of the spectrum for large scattering angles, and LLS becomes identical with hyper-Raman scattering (HRS) of light. The latter phenomenon differs from LLS by several important features. For example, the differential intensity of secondary radiation depends on the first power of the volume, and the radiation frequency in the case of HRS is not an oscillating function of the scattering angle.

It is essential to analyze Ref. 11 in greater detail because the present paper is also based on the idea of the polariton, and it is necessary to elucidate the difference between the present paper and Ref. 11.

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The Hamiltonian for a crystal and radiation interacting with it was written in Ref. 11 in the form

$$H=H_2+W, \tag{1}$$

where H_2 contains second-order terms in the creation and annihilation operators, and W is an operator containing higher-order terms (only third-order terms in Ref. 11). The operator can be written in the form

$$H_2=\sum_{\mathbf{k}j}\hbar|\mathbf{k}|ca_{\mathbf{k}j}{}^+a_{\mathbf{k}j}+\sum_{\mathbf{k}\mu}E_{\mathbf{k}\mu}B_{\mathbf{k}\mu}{}^+B_{\mathbf{k}\mu}$$
$$+\sum_{\mathbf{k}j\mu r}e_r(\mathbf{k}j)\frac{g_r(\mathbf{k}\mu)}{(\hbar|\mathbf{k}|c)^{1/2}}a_{\mathbf{k}j}(B_{\mathbf{k}\mu}{}^++B_{-\mathbf{k}\mu})$$
$$+\sum_{\mathbf{k}j}\frac{\hbar\omega_0{}^2}{4|\mathbf{k}|c}(a_{\mathbf{k}j}a_{-\mathbf{k}j}+a_{\mathbf{k}j}{}^+a_{\mathbf{k}j})+\mathrm{H.c.}, \tag{2}$$

where $E_{\mathbf{k}\mu}$ is the energy of the exciton in the band μ with wave vector $\mathbf{k}$, j labels the photon polarization, $a^+_{\mathbf{k}j}$, $a_{\mathbf{k}j}$, $B^+_{\mathbf{k}\mu}$, $B_{\mathbf{k}\mu}$ are Bose operators for the creation and annihilation of a photon and Coulomb exciton, respectively, $\mathbf{e}(\mathbf{k}j)$ is a unit vector representing the polarization of the field, the index r assumes the values x, y, z, ω_0 is the plasma frequency, and the explicit form of the coefficient $g(\mathbf{k}\mu)$ depends on the model of the crystal that is being used.

The third-order terms examined in Ref. 11 were due to the interaction between charges in the crystal and the field of transverse photons. Their structure is $Q_1(a+a^+)B^+B\sim H_3^{(1)}$. However, the operator describing the interaction between the polaritons, which may contribute to the LLS probability, was not fully taken into account in Ref. 11. It is well known[12] that there are also third-order terms $H_3^{(2)}$ that are due to the Coulomb interaction between excitons (anharmonism in the Coulomb subsystem, in the terminology of Ref. 12). In addition, the contribution of fourth-order terms to the probability of the effect leads to terms of the same order in the creation and annihilation operators, and these were not taken into account in Ref. 11. These terms arise from the operator describing the interaction between particles in the crystal and the radiation field, and anharmonism in the Coulomb subsystem during the transition from Pauli to Bose operators.[13] We shall denote them by $H_4^{(1)}$ and $H_4^{(2)}$, respectively. Moreover, fourth-order terms arise from the operator describing the Coulomb interaction V between excitons even when the kinematic interaction is not taken into account. They will be represented by $H_4^{(3)}$. Fourth-order terms will also arise because of the presence in the Hamiltonian of a term that is quadratic in the vector potential of the field. However, it can be shown that these terms are small in the optical frequency band and will therefore be ignored here. Finally, fourth-order terms arise from the operator describing the behavior of a set of noninteracting molecules because of the presence of the kinematic interaction. They will be represented by $H_4^{(4)}$.

The third- and fourth-order terms discussed above were isolated in Refs. 14 and 15 which were concerned with the theory of HRS. It is clear that, as in the case of HRS, the third-order terms contribute to LLS in the second order of perturbation theory, whereas fourth-order terms contribute in the first order. There are thus seven distinct schemes along which LLS can proceed: the operator $H_3^{(1)}$ in second-order perturbation theory, the operator $H_3^{(2)}$ in second-order perturbation theory, combined effect of the operators $H_3^{(1)}$ and $H_3^{(2)}$, and four schemes involving $H_4^{(n)}$ ($n=1$–4). With these schemes we can associate seven scattering tensors $a^{(n)}$ which are labeled in accordance with the foregoing discussion, but it is not clear *a priori* which of them provides the greatest contribution to the effect. Since Ref. 11 was confined (in our notation) to the tensor $a^{(1)}$, it will be useful to investigate the other six terms. This constitutes our first objective. At first sight, it would appear that these seven tensors cannot be separated. However, it will be shown below that they have different frequency dependence and different form. Consequently, frequency and polarization measurements on LLS can be used to separate contributions due to different scattering mechanisms.

In accordance with the foregoing, anharmonic terms of order three and four in the the exciton operators, which are related to the presence of interactions between excitons, should contribute to the LLS intensity. It will therefore be useful to find the connection between the potential energy of interaction between two excitons and the LLS parameters. This constitutes our second objective.

It is also important to recall Refs. 16 and 17, which reported a determination of nonlinear polarizability tensors or rank 3 and 4. The latter of these is directly related to the LLS amplitude. It was shown that these tensors had poles as $\hbar(\omega_1+\omega_2)$ approached the diexciton band energy. Nevertheless, it is interesting to examine in greater detail the possibility of studying bound states by LLS, and this is the third objective of the present paper. By analogy with the procedure employed in Ref. 18, we use a model Hamiltonian to investigate a system consisting of intramolecular crystal vibrations (vibrational excitons) and photon fields. It will be shown that LLS can be used to determine the energy of the bound states of two dipolar excitons.

§1. MOLECULAR CRYSTALS

Consider the Hamiltonian for a system consisting of a molecular crystal and a radiation field. As we have already noted, it will be written to within the fourth-order terms in the creation and annihilation operators. Second-order terms in operators describing photons and dipolar excitons, and forming the zero-order Hamiltonian, can be represented by (2). After diagonalization by the Bogolyubov-Tyablikov method, they assume the form

$$H_2=\sum_{\mathbf{k}\rho}E_\rho(\mathbf{k})\xi_\rho{}^+(\mathbf{k})\xi_\rho(\mathbf{k}), \tag{3}$$

where $\mathbf{k}$ is the wave vector, ρ is the number of the polariton branch, and $E_\rho(k)$ is the polariton spectrum. The third-order terms are equal to the sum $H_3^{(1)}+H_3^{(2)}$. The operator $H_3^{(1)}$ was examined above, and $H_3^{(2)}$ is due to the presence of the Coulomb interaction between charges in the crystal and contains terms having the structure QB^+BB. The latter operator was written in a similar form in Ref. 12. The fourth-order terms were taken from Ref. 15 and have the form

$Q_2(a + a^+)B^+BB + Q_3B^+B^+BB$. Thus, the complete Hamiltonian for the system takes the form of the sum of second- and higher-order terms in the creation and annihilation operators. In accordance with the ideas exploited in the description of the system by approximate second quantization (see, for example, Ref. 19), this means that the Hamiltonian for the system has been expanded in powers of nN^{-1}, where n, is the number of quasiparticles in the crystal and N is the number of unit cells in it.

If we use the explicit form of H_3, H_4, which can be borrowed from Refs. 12, 15, and 20, we obtain the following expression for the flux of radiation scattered within the solid angle dO and spectral interval between ω_4 and $\omega_4 + d\omega_4$:

$$\frac{\partial^2 S}{\partial\omega_4\partial O}=BI_1I_2\left|\sum_{lmnp} e_l(\mathbf{k}_4j_4)e_m(\mathbf{k}_3j_3)e_n(\mathbf{k}_2j_2)e_p(\mathbf{k}_1j_1)a_{lmnp}\right|^2, \tag{4}$$

where

$$B=\frac{n_4n_3\omega_4{}^2\omega_3L_xL_yS_z}{n_1n_2\omega_1{}^2\omega_2{}^2\cdot 2\pi c^8\hbar^5v_0{}^2},\qquad S_z=\frac{4}{(\Delta k_z)^2}\sin^2\left(\frac{\Delta k_zL_z}{2}\right), \tag{5}$$

$\Delta\,\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4$, l, m, n, p independently assume the values x, y, z, I_i $(i = 1{,}2)$ are the pump intensities (it is assumed that the crystal is illuminated by an infinitesimally narrow line), V is the scattering volume, ω_1,ω_2 are the pump frequencies, ω_3, ω_4 are the scattered radiation frequencies, v_0 is the volume of the unit cell of the crystal, n_i, $\mathbf{k}_i$ $(i = 1{,}2{,}3{,}4)$ are the refractive index and wave vector of the polariton mode of frequency ω_i, respectively, and a_{lmnp} is the LLS tensor. It has been assumed in the derivation of (4) that the crystal is in the form of a parallelepiped with edges L_x, L_y, L_z parallel to the x, y, z axes, and $\mathbf{k}_3$ is parallel to the z axis.

If we take all seven mechanisms described in the Introduction into account, we can write the LLS tensor in the form

$$a_{lmnp}=\sum_{i=1}^{7} a_{lmnp}^{(i)}. \tag{6}$$

Since, as we have already noted, the complete expression for the tensor a is exceedingly cumbersome, and in order to give it a more manageable form, we shall confine our attention to those terms that are important when ω_1, ω_2, ω_3, ω_4 approach the frequencies of exciton absorption bands. Moreover, we shall assume that the crystal has a center of inversion and the unit cell contains a single molecule. The formulas for $a^{(i)}$, obtained under these simplifying assumptions, are given in the Appendix. It is important to note that $a^{(6)}$ vanishes in crystals with a center of inversion because it contains as a factor a tensor of rank three, which is similar to the tensor corresponding to the generation of the second harmonic. The term $a^{(6)}$ will therefore be omitted.

We also note that the LLS effect can, in general, compete with a sequence of two processes. The first is photon absorption with the creation of an exciton, and the second is the decay of this exciton into two photons. This two-step process occurs when the total energy of the two photons is equal to the energy of the exciton. We shall confine our attention in this paper to the situation where this sum differs from the energy of the exciton. Consequently, the conditions under which LLS is examined in this paper preclude the possibility of its being treated as a two-step process.

Since the LLS tensor consists of a series of terms, we must now estimate their relative importance.

Let us begin by considering the contribution due to fourth-order terms in the polariton operator. For the sake of simplicity, we shall suppose that the crystal contains only two exciton bands of excited states, and we shall also suppose that $\omega_1 = \omega_2 = \omega$ and take into account only the first terms in (A.1)–(A.6). As a result, we obtain

$$\frac{a^{(7)}}{a^{(4)}}\sim\frac{E_{\mu_1}}{(E_{\mu_1}-\hbar\omega)},\quad\frac{a^{(4)}}{a^{(5)}}\sim\frac{E_{\mu_1}-\hbar\omega}{V}, \tag{7}$$

$$\frac{a^{(1)}}{a^{(2)}}\sim\frac{2m}{c^2\hbar^2}(\chi_{0\,\mu_1}\chi_{0\,\mu_2})\,(E_{\mu_1}E_{\mu_2})\frac{(E_{\mu_1}-\hbar\omega)\,(E_{\mu_2}-2\hbar\omega)}{V}, \tag{8}$$

$$\frac{a^{(1)}}{a^{(3)}}\sim\frac{(2m)^{1/2}}{e\hbar}(\chi_{0\,\mu_1}E_{\mu_1})^{-1/2}\frac{(E_{\mu_1}-\hbar\omega)}{V}\Biggr),\quad\frac{a^{(1)}}{a^{(4)}}\sim 1, \tag{9}$$

where $\chi_{0\mu}$ is the oscillator strength, e, m are the charge and mass of the electron, and V is the intermolecular interaction.

The approximate formulas given by (7)–(9) show that it is essential to take into account all the terms of the LLS tensor and that they can be separated on the basis of the dependence of intensity on the frequencies ω_i $(i = 1–4)$. We have used these expressions to analyze the following situations that appear to us to be most interesting: (a) the frequencies ω and 2ω are well separated from the absorption bands, (b) the frequencies ω and 2ω are close to the dipole-allowed exciton band, and (c) the frequency 2ω is close to the dipole-forbidden exciton band. The terms $a^{(7)}$, $a^{(4)}$, $a^{(1)}$ are important for case (a). The terms $a^{(2)}$ and $a^{(1)}$ predominate in cases (b) and (c), respectively.

Thus, for a molecular crystal, we must, in general, take into account all seven terms $a^{(i)}$ $(i = 1–7)$ rather than confine our attention to $a^{(1)}$, as was done in Ref. 11.

We now turn to the form of the tensors $a^{(i)}$ $(i = 2–7)$. The first of these need not be investigated because the corresponding tables are given in Ref. 21. We therefore begin with the tensor $a^{(7)}$, which is simplest to analyze. It is clear from (A.6) that it constitutes a Krönecker product of two tensors of rank two, whose form is identical with that of the Rayleigh scattering tensor for which tables are available in the literature (see, for example, Ref. 12). This enables us to find the form of $a^{(7)}$ without difficulty. The form of the tensors given by (A.2)–(A.6) can be examined by analogy. For example, (A.10), which appears as a factor in (A.6), has the same form as the Raman scattering tensor, and (A.11) has the same form as the tensor describing the generation of the second harmonic. The form of these tensors can also be taken from Ref. 12. By performing the appropriate multiplication of (A.7)–(A.12), and using the lattice sums given in Ref. 22, we obtain the form of the tensors given by (A.2)–(A.6).

By applying the above procedure to all five tensors, we can generate tables similar to those given in Ref. 21. However, these tables are very cumbersome and the procedure for finding the tensors reduces to a simple multiplication of expressions available in the literature. There is therefore little point in reproducing the corresponding results here. Nevertheless, a number of general remarks will not be out of place. All components of tensors with $n = 2,3,5$ are nonzero. This is so because they contain as factors the lattice sums that are tensors of rank two, and all components of these tensors are different from zero. Tensors with $n = 4$ or 7 do not contribute new nonzero components as compared with $a^{(1)}$. Consequently, these tensors can be separated experimentally for a number of crystal classes by suitably choosing the geometry of the experiment.

For example, it is desirable to isolate the situation where terms with $n = 2,3,5$, due to the presence of the intermolecular interaction, provide a contribution to the effect. It follows from the foregoing and the tables given in Ref. 21 that, for example, this idea can be implemented for crystals belonging to the groups O, T_d, T, C_{4v}, D_4, D_{3h}, D_6, C_{2v}, D_2 under the following geometry of the experiment: $\mathbf{s}_1(0,0,1)$, $\mathbf{s}_2(1,0,0)$, $\mathbf{s}_4(0,1,0)$, $\mathbf{e}_1(1,0,0)$, $\mathbf{e}_2(0,1,0)$, $\mathbf{e}_4(0,0,1)$, $\mathbf{s} = \mathbf{k}/|\mathbf{k}|$, where $\mathbf{e}$ is the polarization vector. However, for crystals belonging to the groups C_{6h}, C_6, C_4, C_3, C_2, C_{2h}, D_3, C_{3v}, D_{3d}, C_{4h}, the isolation of the intermolecular interaction by polarization measurements turns out to be difficult.

Moreover, the experimental separation of the above tensors can be achieved by measuring the LLS excitation spectra because (A.1)–(A.6) have different frequency dependence.

It will now be useful to examine the possibility of finding the potential energy of interaction $V(\mathbf{R})$ between two excitons by measuring the LLS parameters. We shall consider one of the simplest situations in which only one nondegenerate exciton level is important, and the operator for the interaction between the polaritons reduces to $H_4^{(3)}$. When the level just mentioned lies well away from other levels, and the intermolecular interaction is small, the coefficients of the transformation from molecular variables to exciton variables $u_{f\mu}$ can be set equal to unity in the Heitler-London approximation.[20] When the above assumptions are valid, the corresponding anharmonic constant $Q_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = Q_4(\mathbf{k}_1 - \mathbf{k}_2)$ depends on a single argument. The potential energy of the interaction between the two excitons in which we are interested is then given by

$$V(R)=\frac{1}{(2\pi)^3}\int e^{i\mathbf{kR}}Q_4(\mathbf{k})\,d^3\mathbf{k}, \tag{10}$$

where the integration with respect to the vector $\mathbf{k}$ is performed within the limits of the Brillouin zone, and the values of $Q_4(\mathbf{k})$ must be known for the entire zone before $V(\mathbf{R})$ can be found.

We shall suppose that $\omega_1 = \omega_2 = \omega_3 = \omega$ and bring ω close to $\omega_\mu = E_\mu \hbar^{-1}$. The intensity is then given by (7), in which the role of the LLS tensor is played by the quantity

$$a_{lmnp}=Q_{4\mu\mu\mu\mu}(\mathbf{k}_1-\mathbf{k}_3)$$
$$\times(E_\mu-\hbar\omega)^{-4}g_l(\mathbf{k}_1\mu)\,g_m(\mathbf{k}_2\mu)\,g_n(\mathbf{k}_3\mu)\,g_p(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3\mu). \tag{11}$$

It is clear from (4) and (11) that the sign of $Q_{4\mu\mu\mu\mu}$, which would enable us to settle the question as to whether the excitons attract or repel, cannot be determined and, moreover, it is difficult to reach the region of large values of k because the wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ in (11) lie in the optical part of the spectrum. Thus, even in the simple case determined above, it is difficult to formulate an experimental procedure that would enable us to find $V(\mathbf{R})$. Still greater difficulties are encountered in the analysis of more complicated interactions between the excitons. Nevertheless, the presence of attraction or repulsion can be judged by examining effects in the LLS spectrum that are due to bound states of two excitons, and such considerations support the presence of attraction. This question is examined in the next section.

§2. BOUND STATES

We shall now examine the possibility of using LLS to determine the energy of the bound state formed by two excitons. Following Ref. 18, we shall consider excitons generated by internal dipole-active vibrations of the molecules constituting the crystal. The anharmonic interaction operator, which ensures the presence of both bound states and the LLS effect, will be written in the form

$$W=Q\sum_n B_n^+B_n^+B_nB_n, \tag{12}$$

where Q is the anharmonic constant and B_n^+, B_n are operators describing creation and annihilation of the vibrational excitation of the n-th molecule. It is assumed in (12) that the unit cell of the crystal contains only one molecule which supports only one nondegenerate vibration.

The operator given by (12) must be written in terms of polariton creation and annihilation operators. Several simplifying assumptions are made during the transformation from them to the operators B_n^+, B_n.

First, we confine our attention to the Heitler-London approximation and, secondly, we assume that the frequencies ω_i $(i = 1$–$4)$ lie close to the frequency $\hbar^{-1}E_\mu$ of the above vibration. The operator (12) can then be writen in the form

$$W=\sum_{\mathbf{Kpq}} A^*(\mathbf{K},\mathbf{q})\,A(\mathbf{K},\mathbf{p})\,\xi^+(\mathbf{K}-\mathbf{q})\,\xi^+(\mathbf{q})\,\xi(\mathbf{K}-\mathbf{p})\,\xi(\mathbf{p}), \tag{13}$$

where

$$A(\mathbf{K},\mathbf{p})=u(\mathbf{p})\,u(\mathbf{K}-\mathbf{p})\,(Q/N)^{1/2}, \tag{14}$$

N is the number of unit cells in the periodic volume of the crystal, and $u(\mathbf{p})$ are the coefficients of the transformation from the exciton to the polariton operators. The subscript labeling the exciton band is omitted because there is only one such band; the index of the polariton branch is also omitted because, under the above assumptions, only one such branch is important. The coefficients of the transformation from the states of isolated molecules to the exciton states do not appear in (13) because they are all equal to unity in this case.

Instead of the transition $\mathbf{k}_1, \mathbf{k}_2 \rightarrow \mathbf{k}_3, \mathbf{k}_4$, which is examined in the last section, we consider $\mathbf{Kp} \rightarrow \mathbf{Kq}$, where $\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2$, $\mathbf{p} = \mathbf{k}_1 - \mathbf{k}_2$, $\mathbf{q} = \mathbf{k}_3 - \mathbf{k}_4$, and the matrix element of this transition, including the infinite number of perturbation theory terms, can be written in the form[23]

$$U(\mathbf{K},\mathbf{p},\mathbf{q})=A(\mathbf{K},\mathbf{p})A^*(\mathbf{K},\mathbf{q})+A(\mathbf{K},\mathbf{p})$$
$$\times\Big[\sum_{\mathbf{rs}}A^*(\mathbf{K},\mathbf{r})D(E_0,\mathbf{K},\mathbf{r},\mathbf{s})A(\mathbf{K},\mathbf{s})\Big]A(\mathbf{K},\mathbf{q}). \tag{15}$$

In this expression, $E_0 = \hbar\omega_1 + \hbar\omega_2$ is the energy of the initial state of the system and

$$D(E, \mathbf{K}, \mathbf{r}, \mathbf{s}) = -i \int e^{iE\tau} d\tau \langle 0 | T\xi(\mathbf{r}, \tau)\, \xi(\mathbf{K}-\mathbf{r}, \tau)\, \xi^{+}(\mathbf{s}, 0)\, \xi^{+}(\mathbf{K}-\mathbf{s}, 0) | 0 \rangle \tag{16}$$

is the Fourier transform of the two-particle polariton Green function. The energy parameter E is omitted from (15) and (16) but, in the final expressions, the E-dependence of the various quantities must be borne in mind.

The Green function (16) satisfies the following Dyson equation:

$$D(\mathbf{K}, \mathbf{r}, \mathbf{s}) = D^{(0)}(\mathbf{K}, \mathbf{r})\, [\delta(\mathbf{r}, \mathbf{s}) + \delta(\mathbf{r}, \mathbf{K}-\mathbf{s})] + 2D^{(0)}(\mathbf{K}, \mathbf{r}) \times A(\mathbf{K}, \mathbf{r}) \sum_{\mathbf{x}} A^{*}(\mathbf{K}, \mathbf{x})\, D(\mathbf{K}, \mathbf{x}, \mathbf{s}), \tag{17}$$

where the zeroth Green function is given by

$$D^{(0)}(\mathbf{K}, \mathbf{r}) = \frac{1}{E - E(\mathbf{r}) - E(\mathbf{K}-\mathbf{r})}, \tag{18}$$

and $E(\mathbf{r})$ is the polariton spectrum of the lower branch.

Multiplying (17) from the left by $A^{*}(\mathbf{K},\mathbf{r})$ and from the right by $A(\mathbf{K},\mathbf{s})$, and summing over $\mathbf{r}$ and $\mathbf{s}$, we obtain

$$\Phi = 2\Phi_0 + 2\Phi_0\Phi, \tag{19}$$

where

$$\Phi_0 = \sum A^{*}(\mathbf{K}, \mathbf{r})\, D^{(0)}(\mathbf{K}, \mathbf{r})\, A(\mathbf{K}, \mathbf{r}), \tag{20}$$

$$\Phi = \sum_{\mathbf{pq}} A^{*}(\mathbf{K}, \mathbf{p})\, D(\mathbf{K}, \mathbf{p}, \mathbf{q})\, A(\mathbf{K}, \mathbf{q}). \tag{21}$$

In view of (19)–(21), the matrix element (15) assumes the form

$$U(\mathbf{pq}) = A(\mathbf{K}, \mathbf{p})\, A^{*}(\mathbf{K}, \mathbf{q})\, (1 - 2\Phi_0)^{-1}. \tag{22}$$

The quantity $A(\mathbf{p})$ is known and it is required to find Φ_0. The sum (20) is dominated by values of the wave vector that lie well within the Brillouin zone. The function $U(\mathbf{q})$ for these values can be regarded as independent of $\mathbf{q}$ and can be set equal to unity since, for high values of the wave vector, the lower-branch polariton states can be aproximated by exciton states with sufficient degree of precision. For the same reason, the polariton energy spectrum can be approximately replaced by the exciton spectrum. Thus, with relative precision of the order of $(a\lambda^{-1})^3$, where a is the lattice constant and λ the wavelength of light, we find that

$$\Phi_0 \approx Q/(E - 2\hbar\omega_\mu). \tag{23}$$

It is important to note that the dependence of ω_μ on k was neglected in the derivation of (23).

The formulas given by (22) and (23) determine the transition matrix element and, once this element is known, we can proceed by analogy with the last section to obtain equation (4) for the scattered intensity, where the scattering tensor is given by

$$a_{lmnp}(\omega_1, \omega_2, \omega_3) = \frac{g_l(\omega_\mu, \omega_1)\, g_m(\omega_\mu, \omega_2)\, g_n(\omega_\mu \omega_3)\, g_p(\omega_\mu, \omega_1 + \omega_2 - \omega_3)}{(\omega_\mu - \omega_1)(\omega_\mu - \omega_2)(\omega_\mu - \omega_3)(\omega_\mu - \omega_1 - \omega_2 + \omega_3)} \times \frac{Q}{\omega_1 + \omega_2 - 2\omega_\mu - 2Q}. \tag{24}$$

This tensor has a pole for $\omega_1 + \omega_2 \to \varepsilon_\delta$, where $\varepsilon_\delta = 2\omega_\mu + 2Q$. When $Q < 0$, which corresponds to attraction between the excitons, ε_δ is the energy of the diexciton formed from the two dipolar vibrational states of the molecule. This pole is due to the fact that we have ignored the finite lifetime of the diexciton state. An imaginary component appears when this is taken into account. The final result is that the LLS excitation spectrum contains a peak whose position enables us to determine the energy of the bound state of the two excitons.

Thus, when the anharmonic interaction can be represented by (13), the problem of finding the connection between the LLS excitation spectrum and the bound state energy has the above accurate solution.

A similar procedure can be used to find the solution when the anharmonic operator is a generalization of (13):

$$W = \sum_{\mathbf{Kpq}} \sum_{\alpha\beta\gamma\tau} A_{\alpha\beta}(\mathbf{K}, \mathbf{p})\, A_{\gamma\tau}^{*}(\mathbf{K}, \mathbf{q})\, \xi_\alpha^{+}(\mathbf{K}-\mathbf{p})\, \xi_\beta^{+}(\mathbf{p})\, \xi_\gamma(\mathbf{K}-\mathbf{q})\, \xi_\tau(\mathbf{q}), \tag{25}$$

where α, β, γ, τ assume independently the values corresponding to the numbers of the polariton branches.

To investigate the bound state formed by the two dipole-free excitons, we must assume the presence of an anharmonic interaction between the two dipole-free vibrations and the vibration having a dipole moment. Although an exact solution cannot be obtained for this case, it is, nevertheless, possible to introduce certain specific assumptions and hence conclude that there is a peak on the LLS excitation spectrum whose position can be used to determine the energy of the bound state of the two dipole-free excitons.

The entire foregoing discussion was concerned with the case where anharmonism in the isolated molecule plays a dominant role. However, it is clear that situations in which other interactions between polaritons play a dominant role are of no lesser interest.

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APPENDIX

The components of the LLS tensor have the form

$$a_{lmnp}^{(1)} = b_{lmnp}(\omega_1, \omega_2, \omega_1 + \omega_2) + \ldots, \tag{A.1}$$

$$a_{lmnp}^{(2)} = \sum_{x_1 y_1 x_2 y_2} A_{x_1 y_1}(\mathbf{k}_2)\, A_{x_2 y_2}(\mathbf{k}_4)\, b_{p x_2}^{(\delta)}(\omega_4) \times h_{l y_1 y_2 n}(\omega_1, \omega_3, \omega_1 + \omega_2)\, b_{p x_1}^{(\delta)} + \ldots, \tag{A.2}$$

$$a_{lmnp}^{(3)} = -\sum_{xy} A_{xy}(\mathbf{k}_4)\, b_{py}^{(\delta)}(\omega_4)\, b_{lmxn}(\omega_1, \omega_3, \omega_1 + \omega_2) + \ldots, \tag{A.3}$$

$$a_{lmnp}^{(4)} = b_{lm}^{(\gamma)}(\omega_1)\, b_{np}^{(\beta)}(\omega_3, \omega_4) + \ldots, \tag{A.4}$$

$$a^{(5)}_{lmnp}=\sum_{xy} A_{xy}(\mathbf{k}_1)\, b^{(\delta)}_{lx}(\omega_1)\, b^{(\beta)}_{mn}(\omega_2, \omega_3)\, b^{(\delta)}_{py}(\omega_4)+\ldots, \tag{A.5}$$

$$a^{(7)}_{lmnp}=b^{(\alpha)}_{lp}(\omega_1, \omega_4)\, b^{(\beta)}_{mn}(\omega_2, \omega_3)+\ldots, \tag{A.6}$$

where

$$b^{(\alpha}_{lp}(\omega_1, \omega_2)=\sum_{\mu} R_{0\,\mu}{}^{l}(\omega_1) R_{\mu\,0}{}^{p}(\omega_4) E_{\mu}, \tag{A.7}$$

$$b^{(\beta)}_{mn}(\omega_1, \omega_2)=\sum_{\mu} R_{0\,\mu}{}^{m}(\omega_2) R^{n}_{\mu\,0}(\omega_3), \tag{A.8}$$

$$b^{(\gamma)}_{lm}(\omega_1)=\sum_{\mu} R_{0\,\mu}{}^{l}(\omega_1) P_{\mu\,0}{}^{m} E_{\mu}, \tag{A.9}$$

$$b^{(\delta)}_{lx}(\omega_1)=\sum_{\mu} R_{0\,\mu}{}^{l}(\omega_1) P_{\mu\,0}{}^{x}, \tag{A.10}$$

$$b_{lmnp}=(\omega_1, \omega_2, \omega_3)=\sum_{\mu_1\mu_2} R_{0\,\mu}{}^{l}(\omega_1) I_{\mu_1\mu_2} I^{p}_{\mu_2\mu_3} R_{\mu_3\,0}(\omega_2)(E_{\mu_2}-\hbar\omega_3)^{-1},$$

$$R^{l}_{0\,\mu}(\omega)=P^{l}_{0\,\mu} E_{\mu}(E_{\mu}-\hbar\omega)^{-1},$$

$$I^{m}_{\mu_1\mu_2}=|E_{\mu_1}-E_{\mu_2}| P^{m}_{\mu_1\mu_2}.$$

The index labels the exciton ground state, $\mathbf{P}_{\mu_1\mu_2}$ is the matrix element of the exciton dipole moment operator of the molecule for transition between a state μ_1 to a state μ_2,

$$A_{xy}(\mathbf{k})=\sum_{n} \exp(i\mathbf{k}\mathbf{r}_{0\,n})\,[\delta_{xy}|\mathbf{r}_{0\,n}|^{2}-3x_{0\,n}y_{0\,n}]^{2}|\mathbf{r}_{0\,n}|^{-5},$$

$|\mathbf{r}_{0n}| = (x^2_{0n} + y^2_{0n} + z^2_{0n})^{1/2}$ is the separation between the zeroth unit cell at the origin and the n-th cell, and repeated dots represent the remaining resonance terms that have a similar structure and have been omitted for the sake of simplicity.

[1] E. M. Lifshitz and L. P. Pitaevskii, Relativistic Quantum Theory, Part 2, Pergamon, 1974.

[2] A. A. Grinberg, E. M. Ryvkin, I. M. Frishman, and I. L. Yaroshetskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **7**, 324 (1968) [JETP Lett. **7**, 253 (1968)].

[3] J. G. Meodors, W. T. Kavage, and E. K. Damen, Appl. Phys. Lett. **14**, 360 (1969).

[4] D. L. Weinberg, Appl. Phys. Lett. **14**, 32 (1969).

[5] R. I. Sokolovskii, Zh. Eksp. Teor. Fiz. **59**, 799 (1970) [Sov. Phys. JETP **32**, 438 (1971)].

[6] Yu. M. Kirin, S. G. Rautian, A. E. Semenov, and V. M. Chernoborod, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 340 (1970) [JETP Lett. **11**, 226 (1970)].

[7] Yu Duy Phach, A. Bivas, B. Hönelagi, and L. B. Grun, Phys. Status Solidi B **30**, 159 (1978); H. Schrey, V. G. Lejssenko, and C. Klingshirn, Solid State Commun. **31**, 209 (1979).

[8] H. R. Robl, Quantum Electronics, Columbia Press, New York, 1964, p. 1675; Proc. Third Intern. Congress, Paris.

[9] D. N. Klyshko, Zh. Eksp. Teor. Fiz. **55**, 1006 (1968) [Sov. Phys. JETP **28**, 522 (1969)].

[10] B. Ya. Zel'dovich, Zh. Eksp. Teor. Fiz. **58**, 1348 (1970) [Sov. Phys. JETP **31**, 723 (1970)].

[11] V. L. Strizhevskiĭ and V. V. Obukhovskiĭ, Zh. Eksp. Teor. Fiz. **58**, 929 (1970) [Sov. Phys. JETP **31**, 500 (1970)].

[12] L. N. Ovander, Usp. Fiz. Nauk **86**, 3 (1965) [Sov. Phys. Usp. **8**, 337 (1965)].

[13] B. S. Toshich, Fiz. Tverd. Tela (Leningrad) **9**, 1713 (1967) [Sov. Phys. Solid State **9**, 1346 (1967)].

[14] Yu. D. Zavorotnev and L. N. Ovander, Phys. Status Solidi B **68**, 443 (1975).

[15] Yu. D. Zavorotnev and L. N. Ovander, Fiz. Tverd. Tela (Leningrad) **16**, 3713 (1974) [Sov. Phys. Solid State **16**, 2413 (1975)].

[16] V. M. Agranovich, N. A. Efremov, and E. P. Kominskaya, Opt. Commun. **3**, 387 (1971).

[17] N. A. Efremov and E. P. Kaminskaya, Fiz. Tverd. Tela (Leningrad) **14**, 1185 (1972) [Sov. Phys. Solid State **14**, 1012 (1973)].

[18] V. M. Agranovich and I. I. Lalov, Fiz. Tverd, Tela (Leningrad) **13**, 1032 (1971) [Sov. Phys. Solid State **13**, 859 (1971)].

[19] N. N. Bogolyubov, Izbrannye trudy v trekh tomakh, T.2. Lektsiĭ po kvantovoĭ statistike (Collected Papers in Three Volumes, Vol. 2, Lectures on Quantum Statistics), Naukova Dumka, Kiev, 1970.

[20] V. W. Agranovich, Teoriya eksitonov (Theory of Excitons), Nauka, Moscow, 1968.

[21] S. K. Karpenko and V. L. Strizhevskiĭ, Kvantovaya elektronika (Quantum Electronics), Naukova Dumka, Kiev, 1969, p. 276.

[22] M. Born and M. Bradburn, Proc. Cambr. Phyl. Soc. **39**, 104 (1942).

[23] A. B. Migdal, Kachestvennye metody v kvantovoi teorii (Approximate Methods in Quantum Theory), Nauka Moscow, 1975.

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