

## THEORY OF BOUND EXCITON STATES

M. A. KOZHUSHNER

Institute of Chemical Physics, USSR Academy of Sciences

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The bound states of two quasiparticles which can be effectively described in the lattice-site representation—that is, Frenkel excitons, electrons and holes, and optical phonons—are considered. Equations are derived which give the energy levels of the bound states. The general case of different types of coupling between the quasiparticles is considered, where the kinematic interaction between them is taken into account exactly. It is shown that the bound states divide into two types: symmetric and anti-symmetric. Schemes are presented for the calculation of the bound states for different structures of the energy bands of the bound excitons. It is shown that for certain structures of the energy bands an arbitrary interaction may lead to the presence of a bound state in the three-dimensional case. A one-dimensional model of a vibron excitation—a bound state of an exciton and an optical phonon—is treated in detail. It is shown that the kinematic interaction leads to the result that even in the one-dimensional case, in order to obtain a bound state of two quasiparticles, their dynamic interaction must be sufficiently strong.

## 1. INTRODUCTION

THE possible existence of the bi-exciton, i.e., a bound state of two excitons, was first considered in articles by Moskaleiko and Lampert in 1958.<sup>[1,2]</sup> The bound states of excitons formed out of vibrational and rotational excitations of the H<sub>2</sub> molecule in solid hydrogen were subsequently considered in article<sup>[3]</sup>. Interest in the investigation of such states has constantly increased since then because, in the first place, they give a contribution to the spectral characteristics of crystals and, in the second place, such bound states turn out to have an important effect on the Bose condensation of an exciton gas.<sup>[4,5]</sup>

The bound states of two quasiparticles, which do not necessarily have to be excitons, are investigated in the present work. By quasiparticles we shall understand formations whose wave functions can be written in the form of a linear combination of lattice-site functions (i.e., Wannier functions). Thus, the quasiparticles will be an electron in the conduction band or a hole in the valence band, a Frenkel exciton, or an optical phonon associated by its origin with an intramolecular vibration. But a Wannier exciton is not a quasiparticle in our sense, but rather it is a bound state of two quasiparticles: an electron and a hole. Therefore, a bound state of two Wannier excitons (four quasiparticles) is not considered in our work, but a bound state of two Frenkel excitons (two quasiparticles) is treated.

The coupling of the two quasiparticles may be due to two reasons. In the first place, it may be due to the direct interaction between them, for example, the Coulomb interaction between electron and hole, the van der Waals interaction between two Frenkel excitons, or the exchange interaction between two excitons, for example, between an electronic exciton and an optical phonon.<sup>[6,7]</sup> In the second place, coupling is possible via an intermediate quasiparticle. The coupling of two optical phonons, corresponding to the coupling of the first excited vibrational level of a molecule in the crystal with the second

excited vibrational level of the molecule, may serve as an example of the second type of coupling. Without taking this interaction into account, as a rule the second vibrational excitation will be localized; however the interaction leads to a delocalization of the excitation—it acquires the character of a phonon whose energy is close to the doubled energy of the phonon from the first vibrational excitation, and it may be regarded as a bound state of two such phonons. The theory of such states has been developed in a recent article by Agranovich<sup>[8]</sup> based on an expansion in powers of a small parameter—the ratio of the energy of anharmonicity to the phonon energy. As shown in<sup>[9]</sup>, the second type of coupling between an electron and a hole (via the Frenkel exciton) in crystals of naphthalene and benzene gives an important contribution to the energy of the Frenkel excitons. We also need to take such coupling into account correctly in connection with the investigation of vibronic excitations—bound states of an exciton (or an electron or a hole) with an optical phonon.<sup>[6]</sup>

The general case when both types of exciton coupling are present was considered in the article by Philpott.<sup>[10]</sup> Nonorthogonal functions were used as the basis functions in order to diagonalize the Hamiltonian, where their non-orthogonality is related to the fact that it is impossible for two excitons to stay on one and the same site, i.e., the so-called kinematic repulsion. We shall also consider the general case of the coupling of two excitons, and from the very beginning we shall consistently take the kinematic repulsion of the excitons into account exactly. Our method resembles the method for determining the bound states of spin waves in a ferromagnetic.<sup>[11]</sup> Taking the kinematic repulsion into consideration is very essential; thus, for example, it leads to the result that in the one-dimensional case there is a lower limit on the magnitude of the interexciton interaction at which a bound state appears (see Sec. 5). Here the sign of the interaction is unimportant: for repulsion the energy of the bound bi-exciton state falls into the forbidden band above the band for two free excitons, and for attrac-

tion it falls below this band. The kinematic repulsion identically hinders the formation of both the one and the other bound state.

The problem is solved exactly in the two-exciton approximation. One cannot take three-, four-, and higher exciton states into account since it is assumed that all of the binding energies participating in the problem are much smaller than the exciton energy of an exciton. If coupling via an intermediate exciton is not present, then very frequently the matrix elements of the coupling between the two- and three-exciton states turn out to be small, which also permits a solution of the problem in the two-exciton approximation.

## 2. HAMILTONIAN OF THE SYSTEM AND FORMULATION OF THE PROBLEM

For simplicity we shall consider a crystal lattice having a simple basis. Generalization of the results obtained here to cases of more complicated basis does not present any difficulties.

Let us write down the Hamiltonian for the system under consideration in second-quantized form. Since all of the interactions in the system are two-particle interactions (between two molecules), then the most general form of the Hamiltonian is as follows:

$$\begin{aligned} \hat{\mathcal{H}} = & \epsilon_1 \sum_i a_i^+ a_i + \epsilon_2 \sum_i b_i^+ b_i + \epsilon_3 \sum_i c_i^+ c_i + \sum_{\substack{i, k \\ i \neq k}} \left[ \frac{1}{2} V_{ik}^{(1)} a_i^+ a_k \right. \\ & + \frac{1}{2} V_{ik}^{(2)} b_i^+ b_k + \frac{1}{2} V_{ik}^{(3)} c_i^+ c_k + U_{ik}^{(1)} c_i^+ a_i b_k + U_{ik}^{(2)} c_i^+ b_i a_k + \text{h.c.} \left. \right] \\ & + \sum_{\substack{i, k \\ i \neq k}} [B_{ik} a_i^+ a_i b_k^+ b_k + G_{ik} a_i^+ a_k b_k^+ b_i]. \end{aligned} \quad (1)$$

The summation goes over all lattice sites. Here  $a_i^+$  and  $a_i$  are the operators for the creation and annihilation of an excitation—namely, an exciton of the first type at the  $i$ -th site;  $b_i^+$ ,  $b_i$  and  $c_i^+$ ,  $c_i$  are the creation and annihilation operators for excitons of the second and third types;  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$  denote the energies corresponding to the different types of localized excitons. We shall use the name exciton on the  $i$ -th site or localized exciton for an excited state localized on the  $i$ -th lattice site and described by the corresponding Wannier wave function. Since the exciton-phonon interaction is assumed to be weak, hence there are no excitons in the problem which are localized due to lattice deformations, and the adopted terminology does not lead to any confusion. It is assumed that

$$\Delta = \epsilon_3 - (\epsilon_1 + \epsilon_2) \ll \epsilon_1, \epsilon_2, \quad (2)$$

but  $\Delta$  is comparable with the width of the band  $\sim |V_{ik}^{(1)}|$ ,  $|V_{ik}^{(2)}|$ . Since  $|V_{ik}^{(1),(2)}| \ll \epsilon_{1,2}$  for electronic excitons and optical phonons, this does not contradict assumption (2).

The fourth, fifth, and sixth terms on the right-hand side of Eq. (1) are interactions which lead to the transfer of an excitation of the appropriate type from site to site. They lead to delocalization of the excitations and the formation of exciton energy bands. The seventh term in the sum represents the interaction which leads to the formation of excitons of the third type out of ex-

citons of the first and second types, or else leads to its decay. Thus, in the case of coupling between an electron, a hole, and a Frenkel exciton, the quantity  $U_{ik}^{(1)}$  represents the matrix element for the annihilation of an electron at the  $i$ -th site and the annihilation of a hole at the  $k$ -th site with the creation of a localized Frenkel exciton at the  $i$ -th site;  $U_{ik}^{(2)}$  corresponds to the same process, but the exciton is created at that site where the hole was annihilated. In the case of coupling between an electronic exciton and an optical phonon,  $U_{ik}$  denotes the interaction which leads to the creation of a vibron.<sup>[6]</sup> The eighth term in (1) corresponds to the direct coupling between excitons of the first and second types; for Frenkel excitons  $B_{ik}$  is the difference between the van der Waals interaction energy of two excited molecules with each other and the interaction energy of these molecules with an unexcited molecule. For an electron and a hole, the Coulomb interaction is also included in  $B_{ik}$ . The last term corresponds to the exchange coupling, when excitons of both types change places. For identical excitons this term is not present.

Thanks to the inequality (2), in order to calculate the binding energy of two excitons we may seek a wave function which diagonalizes the Hamiltonian (1), in the form of a linear combination of the states corresponding to energies close to  $\epsilon_1 + \epsilon_2 \approx \epsilon_3$ :

$$\Phi = \sum_{i, j} f(\mathbf{r}_i, \mathbf{r}_j) \Psi_{ij} + \sum_i \mu(\mathbf{r}_i) \chi_i, \quad (3)$$

where

$$\Psi_{ij} \equiv a_i^+ b_j^+ |0\rangle, \quad \chi_i \equiv c_i^+ |0\rangle. \quad (4)$$

Here  $|0\rangle$  denotes the unperturbed state of the crystal and  $\mathbf{r}_i$  is the radius vector to the  $i$ -th site. We note that

$$\Psi_{ii} \equiv 0, \quad (5)$$

i.e., no more than one exciton can sit on any single site of the crystal. Let us change to new variables, namely, we introduce the coordinate corresponding to the "center of mass" of the two excitons and the relative coordinate:

$$\mathbf{R} = 1/2(\mathbf{r}_1 + \mathbf{r}_2), \quad \mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2). \quad (6)$$

Owing to the translational invariance of the Hamiltonian (1), the quasimomentum  $\mathbf{K}$  conjugate to the coordinate  $\mathbf{R}$  and corresponding to the motion of the system of excitons as a whole is a constant of the motion, i.e., the eigenfunction of  $\mathcal{H}$  is

$$\Phi(\mathbf{K}) = \sum_{\mathbf{r}} f(\mathbf{K}, \mathbf{r}) \Psi(\mathbf{K}, \mathbf{r}) + \mu(\mathbf{K}) \chi(\mathbf{K}), \quad (7)$$

where  $f(\mathbf{K}, \mathbf{r})$  and so forth are the Fourier transforms of the corresponding functions which were introduced in Eqs. (3) and (4).

It would appear that one might attempt to diagonalize the Hamiltonian (1), like it is done in<sup>[10]</sup>, in the space of the functions  $\tilde{\psi}(\mathbf{k}_1, \mathbf{k}_2) = \psi_1(\mathbf{k}_1) \psi_2(\mathbf{k}_2)$ , where

$$\psi_1(\mathbf{k}_1) = \frac{1}{\sqrt{N}} \sum_i \exp(i\mathbf{k}_1 \mathbf{r}_i) a_i^+ |0\rangle, \quad \psi_2(\mathbf{k}_2) = \frac{1}{\sqrt{N}} \sum_i \exp(i\mathbf{k}_2 \mathbf{r}_i) b_i^+ |0\rangle \quad (8)$$

are the wave functions of noninteracting excitons. However, due to the condition (5) the basis (8) is nonorthogonal (see<sup>[10,12]</sup>). Even though the violation of orthogonality is only  $\sim N^{-1}$ , still the ratio of the phase volume

corresponding to bound states to the phase volume of the unbound excitons is also  $\sim N^{-1}$ . Without encumbering this article with detailed calculations, let us briefly trace the path followed to obtain the final equations for the amplitudes  $f(\mathbf{K}, \mathbf{r})$  and  $\mu(\mathbf{K})$  and for the energy eigenvalues.

By virtue of condition (5) the amplitude  $f(\mathbf{K}, 0)$  does not appear in the equations which are derived from Eqs. (1) and (7). However, as a consequence of this these equations lose symmetry and their solution becomes difficult. Therefore, in the same way in which it is done for the bound states of magnons in ferromagnetics,<sup>[13]</sup> let us assume that  $f(\mathbf{K}, 0)$  is also determined by these equations which relate  $f(\mathbf{K}, \mathbf{r})$  for different values of  $\mathbf{r}$  and  $\mu(\mathbf{K})$ . We note one important property. The Hamiltonian (1) commutes with the inversion operator  $\hat{I}$  which interchanges the positions of excitons of the first and second types. Therefore, the function  $f(\mathbf{K}, \mathbf{r})$  may either be symmetric in  $\mathbf{r}$ :  $f_S(\mathbf{K}, \mathbf{r}) = f_S(\mathbf{K}, -\mathbf{r})$ , or else antisymmetric in  $\mathbf{r}$ :  $f_A(\mathbf{K}, \mathbf{r}) = -f_A(\mathbf{K}, -\mathbf{r})$ ; these functions correspond to the two eigenvalues of the operator  $\hat{I}$ : +1 and -1. If both of the excitons are identical, then  $f(\mathbf{K}, \mathbf{r})$  can only be symmetric:  $f_S(\mathbf{K}, \mathbf{r})$  because  $\Psi(\mathbf{K}, \mathbf{r}) = \Psi(\mathbf{K}, -\mathbf{r})$ . However, in the general case two systems of levels exist, corresponding to symmetric and antisymmetric states.

Changing to the Fourier transform of  $f(\mathbf{K}, \mathbf{r})$  which we denote by  $\tilde{f}(\mathbf{K}, \mathbf{q})$ ,

$$f(\mathbf{K}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \tilde{f}(\mathbf{K}, \mathbf{q}) \exp(i\mathbf{q}\mathbf{r}), \quad (9)$$

we finally obtain

$$\begin{aligned} \tilde{f}_s(\mathbf{K}, \mathbf{q}) &= [\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})]^{-1} N^{-\frac{1}{2}} \left\{ V(\mathbf{K}, \mathbf{q}) f(\mathbf{K}, 0) \right. \\ &- \sum_{\mathbf{n}>0} 2[B(\mathbf{n}) + G(\mathbf{n})] \tilde{f}_s(\mathbf{K}, \mathbf{n}) \cos(\mathbf{q}\mathbf{n}) + \left. \left[ \varepsilon_3 - E + \sum_{\mathbf{n}} V_n^{(3)} \cos(\mathbf{K}\mathbf{n}) \right]^{-1} \right. \\ &\times U(\mathbf{K}, \mathbf{q}) \sum_{\mathbf{n}>0} 2(U_n^{(1)} + U_n^{(2)}) \cos\left(\frac{\mathbf{K}\mathbf{n}}{2}\right) \tilde{f}_s(\mathbf{K}, \mathbf{n}) \left. \right\}, \\ \tilde{f}_a(\mathbf{K}, \mathbf{q}) &= i[\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})]^{-1} N^{-\frac{1}{2}} \left\{ \sum_{\mathbf{n}>0} 2[G(\mathbf{n}) - B(\mathbf{n})] \tilde{f}_a(\mathbf{K}, \mathbf{n}) \right. \end{aligned} \quad (10)$$

$$\begin{aligned} &\times \sin(\mathbf{q}\mathbf{n}) + \left. \left[ \varepsilon_3 - E + \sum_{\mathbf{n}} V_n^{(3)} \cos(\mathbf{K}\mathbf{n}) \right]^{-1} U(\mathbf{K}, \mathbf{q}) \right. \\ &\times \sum_{\mathbf{n}>0} 2(U_n^{(1)} - U_n^{(2)}) \tilde{f}_a(\mathbf{K}, \mathbf{n}) \sin\left(\frac{\mathbf{K}\mathbf{n}}{2}\right) \left. \right\}, \quad (11) \end{aligned}$$

where

$$V(\mathbf{K}, \mathbf{q}) = \sum_{\mathbf{n}} [V_n^{(1)} + V_n^{(2)}] \cos\left(\frac{\mathbf{K}\mathbf{n}}{2}\right) \exp(i\mathbf{q}\mathbf{n}), \quad (12)$$

$$U(\mathbf{K}, \mathbf{q}) = \sum_{\mathbf{n}} \left[ U_n^{(1)} \exp\left(-i\frac{\mathbf{K}\mathbf{n}}{2}\right) + U_n^{(2)} \exp\left(i\frac{\mathbf{K}\mathbf{n}}{2}\right) \right] \exp(i\mathbf{q}\mathbf{n}).$$

With the aid of Eq. (9) systems of linear homogeneous equations for  $f_S(\mathbf{K}, \mathbf{n})$  and  $f_A(\mathbf{K}, \mathbf{n})$  are obtained from Eqs. (10) and (11). Equating the determinants of these systems to zero gives equations for the determination of the bound state energies. For the symmetric states we have

$$\text{Det} |J_{n'n''}^{(s)} - \delta_{n'n''}| = 0, \quad (13)$$

$\mathbf{n}', \mathbf{n}'' = 0, \dots, \mathbf{n}_r$  where  $\mathbf{n}_r$  is equal to half the number

of sites on which the inter-excitonic interaction is being propagated,

$$J_{n_0}^{(s)} = \frac{1}{N} \sum_{\mathbf{q}} [\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})]^{-1} V(\mathbf{K}, \mathbf{q}) \cos(\mathbf{q}\mathbf{n}), \quad (14)$$

$$\begin{aligned} J_{n'n''}^{(s)} (n'' \neq 0) &= \left[ \varepsilon_3 - E + \sum_{\mathbf{n}} V_n^{(3)} \cos(\mathbf{K}\mathbf{n}) \right]^{-1} 2[U_{n''}^{(1)} + U_{n''}^{(2)}] \\ &\times \cos\left(\frac{\mathbf{K}\mathbf{n}''}{2}\right) \frac{1}{N} \sum_{\mathbf{q}} [\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})]^{-1} U(\mathbf{K}, \mathbf{q}) \cos(\mathbf{q}\mathbf{n}') \\ &- \frac{2}{N} \sum_{\mathbf{q}} [\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})]^{-1} [B(n'') + G(n'')] \cos(\mathbf{q}\mathbf{n}'') \cos(\mathbf{q}\mathbf{n}'). \end{aligned}$$

The equation for the energies of the antisymmetric states is

$$\text{Det} |J_{n'n''}^{(a)} - \delta_{n'n''}| = 0, \quad (15)$$

where  $\mathbf{n}', \mathbf{n}'' = \mathbf{n}_1, \dots, \mathbf{n}_r$ ,

$$\begin{aligned} J_{n'n''}^{(a)} &= \frac{2}{N} \sum_{\mathbf{q}} [\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})]^{-1} \left\{ [G(n'') - B(n'')] \sin(\mathbf{q}\mathbf{n}') \right. \\ &\times \sin(\mathbf{q}\mathbf{n}'') + \left. \left[ \varepsilon_3 - E + \sum_{\mathbf{n}} V_n^{(3)} \cos(\mathbf{K}\mathbf{n}) \right]^{-1} [U_{n''}^{(1)} - U_{n''}^{(2)}] \right. \\ &\times \left. \sin\left(\frac{\mathbf{K}\mathbf{n}''}{2}\right) U(\mathbf{K}, \mathbf{q}) \sin(\mathbf{q}\mathbf{n}') \right\}. \quad (16) \end{aligned}$$

From Eqs. (11) and (15) it is clear that the impossibility of having more than one quasiparticle simultaneously occupy one and the same site does not have any effect on the calculation of the antisymmetric states, since  $f(\mathbf{K}, 0) = 0$  by virtue of the symmetry conditions. Therefore, in order to determine the bound antisymmetric states one can use the basis (8). We emphasize that such states are possible only for quasiparticles of different types.

### 3. GENERAL INVESTIGATION OF THE EQUATIONS. SCHEMES FOR AN APPROXIMATE CALCULATION OF THE BOUND STATES

Equations (10) and (11) can be solved rigorously only if the interactions between the excitons are short-ranged, and therefore the rank of the determinants in (13) and (15) is not large. The rank of the determinant, which must be actually calculated, depends on two factors: 1) on the energy of the level which is being calculated, and 2) on whether the interactions  $V_n^{(1)}$  and  $V_n^{(2)}$  forming the one-exciton bands are long- or short-range interactions.

Assume that one can introduce an interaction radius for  $V_n = V_n^{(1)} + V_n^{(2)}$  (i.e.,  $V_n$  falls off faster than  $n^{-3}$ ). Then

$$f(\mathbf{K}, \mathbf{n}) \sim \int \frac{\exp(i\mathbf{q}\mathbf{n})}{\varepsilon_1 + \varepsilon_2 - E + V(\mathbf{K}, \mathbf{q})} d\mathbf{q}, \quad (17)$$

and since in this case the one-exciton band does not have any singularities (see, for example, <sup>[14]</sup>), then  $V(\mathbf{K}, \mathbf{q})$  will also not have any singularities in  $\mathbf{q}$ , and the integral in (17) falls off exponentially with increasing  $n$ :<sup>[15,16]</sup>

$$f(\mathbf{K}, \mathbf{n}) \sim \exp(-\alpha_K n). \quad (18)$$

If we denote the difference in energy between  $E_{\mathbf{K}}$  and the edge of the two-exciton band by  $\delta_{\mathbf{K}}$  and the width of

the two-exciton band by  $\tilde{V}(\mathbf{K})$ , then  $\alpha \sim \delta_{\mathbf{K}}/\tilde{V}(\mathbf{K})$  for  $\delta_{\mathbf{K}} \gtrsim \tilde{V}(\mathbf{K})$  and  $\alpha \sim (\delta_{\mathbf{K}}/\tilde{V}(\mathbf{K}))^{1/2}$  for  $\delta_{\mathbf{K}} \ll \tilde{V}(\mathbf{K})$ .

Since all of the interactions also fall off with increasing  $|n|$ , then by taking (18) into account one can effectively cutoff all of the sums over  $n$  in Eqs. (10) and (11) at some value of  $n$ . It is quite natural that the deeper the level, i.e., the larger  $\delta(\mathbf{K})$ , the smaller the number of terms which must be taken into consideration, and therefore the lower the rank of the corresponding determinant.

It is easy to understand the physical meaning of such a cutoff in the summation over  $n$  since  $f(\mathbf{K}, n)$  is the analog of the wave function of the bound state of two particles, i.e., of the two excitons.<sup>[17]</sup> The change of the interaction potential (in particular, its vanishing) in the region where  $f(\mathbf{K}, n)$  is very small has little influence on the position of the energy level of the bound state whose wave function is  $f(\mathbf{K}, n)$ . Thus, the scheme for the self-consistent calculation of the levels  $E(\mathbf{K})$  will be as follows: 1) we introduce  $\delta_{\min}$ —the lower limit of the values  $\delta_{\mathbf{K}}$  determined by our calculation; 2) starting from  $\delta_{\min}$  we determine  $(\alpha_{\mathbf{K}})_{\min}$  according to formula (17) and, assigning a definite accuracy to the calculation and taking into consideration that  $f(\mathbf{K}, n) \lesssim \exp(-(\alpha_{\mathbf{K}})_{\min} n)$ , we confine our attention to a summation over a finite number of sites  $n$ . The values  $\delta_{\mathbf{K}}$  found from the solutions of (13) and (15) should satisfy the condition  $\delta_{\mathbf{K}} > \delta_{\min}$ . Then the calculation is self-consistent. We note that if  $B(n)$ ,  $G(n)$ , and  $U(n)$  are short-range, then we can immediately determine all of the levels with a specific accuracy by confining our attention to a finite (usually a small) value of  $n$ . If it turns out that  $\delta_{\mathbf{K}} < \delta_{\min}$  then obviously for the correct determination of  $\delta_{\mathbf{K}}$  one should take a larger number of terms into account in the summation over  $n$ . If  $n \gg 1$ , i.e., if the radius of the wave function is considerably larger than the lattice constant, then in Eqs. (10) and (11) one can change from discrete variables  $n$  to continuous variables, and Eqs. (10) and (11) become the usual Schrödinger equations where the effective masses of the particles enter. The appearance of the effective masses is associated with the fact that the condition  $n \gg 1$  means  $\delta_{\mathbf{K}} \ll \tilde{V}(\mathbf{K})$ , i.e., in the calculation one can actually confine one's attention to the behavior of  $V^{(1)}(\mathbf{K})$  and  $V^{(2)}(\mathbf{K})$  near the extrema of the corresponding bands.

If  $V_n^{(1)} + V_n^{(2)}$  has the nature of a dipole-dipole interaction, then as is well-known the exciton bands have a singularity of the type of a finite discontinuity associated with zero quasimomentum. From (12) it is seen that  $V(\mathbf{K}, \mathbf{q})$  will have a singularity in  $\mathbf{q}$  for  $\mathbf{q} = \pm \mathbf{K}/2$ . Then according to (17)  $f(\mathbf{K}, n) \sim n^{-3}$  (see the corresponding integrals in Section 4 of the author's article<sup>[15]</sup>). Since  $B(n)$ ,  $G(n)$  and  $U(n)$  fall off faster than  $n^{-1}$ , then the sums over  $n$  in (10) and (11) converge, and as before we may confine our attention to a finite number of terms in the sums over  $n$ . However, now  $f(\mathbf{K}, n)$  no longer depends on  $\delta_{\mathbf{K}}$  according to (18), but the dependence is more complicated, and  $f(\mathbf{K}, n) \rightarrow \infty$  as  $\delta_{\mathbf{K}} \rightarrow 0$  (see formulas (34) and (35) in<sup>[15]</sup>). Thus, even in the case of short-range interactions  $B(n)$  and  $U(n)$  it is impossible in general to limit ourselves to one and the same value  $n_r$  in order to determine all levels. Calculation of the bound states with  $\delta_{\mathbf{K}} \rightarrow 0$  requires a sum-

mation over an increasingly larger number  $n$ , i.e., the ranks of the determinants in (13) and (15) increase.

One can use just this described calculational scheme in order to investigate the energy spectrum and structure of a Wannier exciton of small radius, when the "hydrogenlike nature" completely vanishes.

Let us consider one interesting special case when an arbitrary interaction, no matter how weak it may be, leads to the formation of a bound state. Let us consider a cubic crystal, and in  $V_n^{(1)}$  and  $V_n^{(2)}$  only the interaction with nearest neighbors is taken into consideration, where for simplicity we assume the interaction to be the same for all six neighbors. Then the structure of the one-exciton band will be

$$\varepsilon_{1,2}(k_{1,2}) = \varepsilon_{1,2} + V_{1,2}[\cos(k_{1,2,d}) + \cos(k_{1,2,d}) + \cos(k_{1,2,d})],$$

and one can easily see that the two-exciton band will be given by

$$\varepsilon(\mathbf{K}, \mathbf{q}) = \varepsilon_1 + \varepsilon_2 + (V^{(1)} + V^{(2)}) \left[ \cos\left(\frac{K_x d}{2}\right) \cos(q_x d) + \cos\left(\frac{K_y d}{2}\right) \cos(q_y d) + \cos\left(\frac{K_z d}{2}\right) \cos(q_z d) \right]. \quad (19)$$

For  $\mathbf{K} = \mathbf{K}^0$ , where  $K_x^0, y, z = \pm \pi/d$ ,  $\varepsilon(\mathbf{K}^0, \mathbf{q}) = \varepsilon_1 + \varepsilon_2 = \text{const}$  and all of the off-diagonal elements in the determinants (13) and (15) vanish. Setting each  $n_{\mathbf{K}}$ -th diagonal element of these determinants equal to zero, we find the energy of the bound state which corresponds to two excitons located at a distance  $n_{\mathbf{K}}$  from each other. For example, for the levels of the symmetric states assuming that  $U^{(1)}, (2)$  also differs from zero only for nearest neighbors, from Eq. (13) we obtain

$$E_{n_{\mathbf{K}}}(\mathbf{K}^0) = \varepsilon_1 + \varepsilon_2 + B(n_{\mathbf{K}}) + G(n_{\mathbf{K}}). \quad (20)$$

From Eq. (15) we obtain a quadratic equation for the determination of the antisymmetric states, and this yields the solution

$$E_{n_{\mathbf{K}}}(\mathbf{K}^0) = \varepsilon_1 + \varepsilon_2 + \frac{\Delta - b}{2} \pm \sqrt{\frac{(\Delta + b)^2}{4} + 2U_{-}^2}, \quad (21)$$

where

$$\Delta = \varepsilon_3 - \sum_n V_n^{(0)} - \varepsilon_1 - \varepsilon_2, \quad b = G(n_{\mathbf{K}}) - B(n_{\mathbf{K}}), \quad U_{-} = (U_{n_{\mathbf{K}}}^{(1)} - U_{n_{\mathbf{K}}}^{(2)}).$$

It is not difficult to show, by considering the solutions of (13) and (15) for  $\mathbf{K}$  near  $\mathbf{K}^0$  ( $|\mathbf{K} - \mathbf{K}^0| \ll \pi/d$ ), that

$$E(\mathbf{K}) = E(\mathbf{K}^0) + \sum_{\alpha, \beta = x, y, z} a_{\alpha\beta}(\mathbf{K} - \mathbf{K}^0)_{\alpha}(\mathbf{K} - \mathbf{K}^0)_{\beta},$$

where the  $a_{\alpha\beta}$  are the coefficients of a quadratic form of fixed sign, i.e., the energy  $E(\mathbf{K})$  has an extremum at the point  $\mathbf{K} = \mathbf{K}^0$  of the reciprocal lattice. Thus, the states (20) and (21) correspond to bi-excitons at rest, since their group velocity is equal to zero. In addition, the excitons themselves in these states also do not move relative to each other, because for the state with energy  $E_{n_{\mathbf{K}}}^1(\mathbf{K}^0)$  the wave function  $f(\mathbf{K}^0, n_{\mathbf{K}}) \sim \delta_{nn_{\mathbf{K}}}$ . Such a type of

phenomenon involving the compulsory occurrence of bound states arise for those values of the total momentum  $\mathbf{K}$  at which the total energy of the two free excitons does not depend on their relative quasimomentum  $\mathbf{q}$ . If both excitons are identical:  $V_n^{(1)} = V_n^{(2)}$  and their energy band  $\varepsilon(\mathbf{k}_{1,2}) = \varepsilon_1 + V^{(1)}(\mathbf{k}_{1,2})$ , where  $V^{(1)}(\mathbf{k}_{1,2})$

$= \sum_n V_n^{(1)} \cos(\mathbf{k}_{1,2} \cdot \mathbf{n})$ , then

$$V(\mathbf{K}, \mathbf{q}) = V^{(1)}\left(\frac{\mathbf{K}}{2} + \mathbf{q}\right) + V^{(2)}\left(\frac{\mathbf{K}}{2} - \mathbf{q}\right). \quad (22)$$

For those values of  $\mathbf{K}$  at which the relation

$$V^{(1)}\left(\frac{\mathbf{K}}{2} + \mathbf{q}\right) = -V^{(2)}\left(\frac{\mathbf{K}}{2} - \mathbf{q}\right), \quad (23)$$

is satisfied, the fixed bi-excitons considered above must appear. In the case of identical excitons it is only necessary to solve Eq. (13). In analogy to (23)  $U(\mathbf{K}^0, \mathbf{q}) = -U(\mathbf{K}^0, -\mathbf{q})$ , then in (14) only the second term is left, and we obtain expression (20) for the energies of the bound states.

**4. ONE-DIMENSIONAL CASE. THE COUPLING OF AN EXCITON WITH A PHONON**

Let us illustrate the solution of Eqs. (13) and (15) in the one-dimensional case where all of the interactions involve interactions with a nearest neighbor. Let us consider the coupling between a Frenkel exciton and an optical phonon—that is, an intramolecular vibration, where the formation of a vibronic exciton is possible (when the exciton and the phonon sit on the same site). This special case was also investigated in [6].

We shall assume that the width of the exciton band is much larger than the width of the phonon band, i.e.,  $V_n^{(1)} \gg V_n^{(2)}$  and therefore  $V_n = V_n^{(1)} + V_n^{(2)} \approx V_n^{(1)}$ . Let us assume that the direct coupling between the exciton and the phonon is guaranteed due to the exchange interaction  $G(n)$ , but  $B(n) = 0$ . Since  $V^{(2)} \ll V^{(1)}$  then it is natural to assume that  $U^{(2)} \ll U^{(1)}$ . Then Eqs. (13) and (15) go over into two equations for the determination of  $E$ :

$$\left[ \frac{4U^2 \cos^2(Kd/2)}{\Delta(K) + (\epsilon_1 + \epsilon_2 - E)} - 2G \right] \frac{1}{\epsilon_1 + \epsilon_2 - E} = \frac{a^2}{1 - \sqrt{1 - a^2}} \quad (24)$$

$$\left[ \frac{4U^2 \sin^2(Kd/2)}{\Delta(K) + (\epsilon_1 + \epsilon_2 - E)} + 2G \right] \frac{1}{\epsilon_1 + \epsilon_2 - E} = \frac{a^2}{1 - \sqrt{1 - a^2}}. \quad (25)$$

Here  $U = U^{(1)}$ ,

$$\Delta(K) = \epsilon_3 + 2V^{(3)} \cos(Kd) - (\epsilon_1 + \epsilon_2), \quad (26)$$

$$a = \frac{2V^{(1)} \cos(Kd/2)}{\epsilon_1 + \epsilon_2 - E}. \quad (27)$$

The bound states correspond to the condition

$$|a| < 1. \quad (28)$$

Equation (24) gives the bound states of symmetric type, and (25) gives the bound states of antisymmetric type. We emphasize that in this one-dimensional case a bound state is possible for arbitrary values of the interaction only when  $K = \pm \pi/d$  (see the previous section), when  $a = 0$ , and from (24) we obtain  $E = \epsilon_1 + \epsilon_2 + G$ , and from (25)

$$E = \epsilon_1 + \epsilon_2 + \frac{\Delta - G}{2} \pm \sqrt{\frac{(\Delta + G)^2}{4} + 2U^2}.$$

For any other values of  $K$  bound states are formed only for a quite definite value of the interactions. Thus, if  $U = 0$ , then from (24) and (25) we obtain

$$\pm \frac{G}{V \cos(Kd/2)} = \frac{a}{1 - \sqrt{1 - a^2}}. \quad (29)$$

Taking (28) into consideration, we obtain the condition for the existence of a bound state:  $|G/V \cos(Kd/2)| > 1$ .

For  $K = 0$  one antisymmetric bound state having an energy  $E = \epsilon_1 + \epsilon_2 - G$  is determined by only the exchange interaction. The amplitude of the vibron excitation in the wave function of this state is equal to zero, and therefore in it an optical transition from the ground state is not possible. However a different antisymmetric state having an energy  $E = \epsilon_3 + 2V^{(3)}$  (purely vibronic) is possible if  $\epsilon_3 + 2V^{(3)}$  is located outside the energy band of the unbound exciton and phonon.

Bound states of symmetric type do not divide into purely vibronic and purely exchange types, but they correspond to a mixture of both states.

Thus, for  $K = 0$  the antisymmetric bound states divide into purely vibronic and purely exchange states. Measuring the energies of these states, we may accordingly separately determine  $\Delta = \epsilon_3 - (\epsilon_1 + \epsilon_2)$  and  $G$ . This conclusion is common not only for the one-dimensional case but also for a three-dimensional problem.

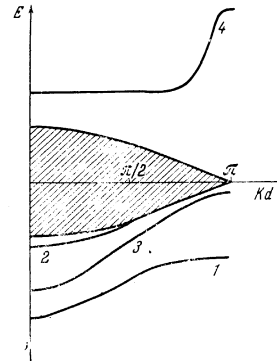
From (24) and (25) it is clear that for

$$\left| \frac{2V \cos(Kd/2)}{\Delta(K)} \right| < 1$$

there will always be two bound states, but in the general case not more than four bound states are possible, and for  $K = \pm \pi/d$  only three bound states are possible. A typical picture of the dependences of the energies of the bound states is shown in the accompanying figure. The calculation was made for  $U^{(1)}/V^{(1)} = \Delta/2V^{(1)} = V^{(3)}/V^{(1)} = 1$ ,  $G/3V^{(1)} = 1$ , and  $V^{(1)} < 0$ . The cross-hatched region represents the energy of the unbound exciton and phonon. Curves 1 and 2 indicate the energy levels of the symmetric states, curves 3 and 4 correspond to the antisymmetric states, where curve 3 represents a purely vibronic state for  $K = 0$ , and curve 4 represents a pure exchange state.

**5. CONCLUSION**

The bound states of two excitons have been considered for a general type of coupling between them. The only restriction is the smallness of the binding energy in comparison with the excitation energy of any of the excitons. The kinematic interaction between the excitons is rigorously taken into consideration. It is shown that bound states of two types exist—symmetric and antisym-



metric—and algebraic equations (13) and (15) are obtained for the determination of the energy levels and, correspondingly, for the determination of the wave functions of these states. A scheme is given for the calculation of the bound states even in the presence of long-range interactions between the excitons. The scheme of calculation essentially depends on the analytic dependence of  $\epsilon(\mathbf{k})$  for the excitons whose bound states are being considered. Thus one can consider Wannier excitons of small radius. It is shown that in certain cases, for example, in a cubic lattice with exciton bands being formed by the interaction with only nearest neighbors, bound states of two excitons are always possible. A one-dimensional model of the coupling of an exciton with an optical phonon is considered in detail.

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