SOVIET PHYSICS JETP VOLUME 5, NUMBER 1 AUGUST,1957

The Exciton State of an Imperfect Molecular Crystal

A. S. SELIVANENKO
P. N. Lebedev Physical Institute, Academy of Sciences, USSR

(Submitted to JETP editor July 12, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 75–81 (1957)

The Schrödinger equation is solved in a semi–infinite molecular crystal. Exciton states localized at the surface are found. The energy spectrum of surface excitons is obtained.

I. INTRODUCTION

A. S. DAVYDOV[1] investigated the excited states (given the name "excitons" by Ia. I. Frenkel') of an ideal molecular crystal. If the number of elementary cells in the perfect crystal is large, it is obviously permissible to regard the crystal as infinite and to impose periodic boundary conditions.

It has been shown theoretically[2] that in a large crystal the finiteness of the volume, if taken into account accurately, does not lead to a noticeable disturbance of the normal motions. But the assumption that a crystal is infinite necessarily makes it impossible to investigate physical phenomena occurring at the surface. Very few papers[3] have been written on this subject, mainly because the disturbance produced by the free crystal surface is not small compared with the molecular interaction energy, and therefore ordinary perturbation theory is inapplicable. I. M. Lifshitz's theory of regularly degenerate perturbations[4–7] makes possible some significant progress in this direction.

Our problem is to study the behavior of an excited state (exciton) at the surface of a molecular crystal. For simplicity we consider a cubic lattice with one molecule per unit cell. We neglect the molecular motions, i.e., we study a "free' exciton. The equation for a stationary state of a molecular crystal can be written in the form

$$\Big(\sum_n \hat{H}_n + \frac{1}{2}\sum_{nm}{}' \hat{V}^0_{nm} - \mathcal{E}\Big)\Phi = 0, \tag{1}$$

where $\hat{H}_n$ is the energy operator of the molecule in the n'th cell of the lattice, $\hat{V}^0_{nm}$ the interaction operator between the m'th and n'th molecules, $\mathcal{E}$ the eigenvalue, and Φ the wave–function of the crystal. The summation extends over all molecules in the crystal, and the prime means that the terms with $n = m$ are omitted. The molecules are bound by Van der Waals forces, and the binding energies are much smaller than the dissociation energy of a molecule. These properties are indicated by the fact that, when a molecular crystal sublimes, the molecules evaporate without dissociation. The weak binding of the molecules in the crystal preserves to some extent the individuality of each molecule and allows us to use the most powerful method of calculation, perturbation theory.

Since $\hat{V}^0_{nm}$ is small, an approximate wave-function for the crystal can be expressed in the form

$$\Phi = \varphi_{-N} \cdots \varphi_{-1}\varphi_0\varphi_1 \cdots \varphi_N = \prod_m \varphi_m.$$

Here $(2N_1 + 1)(2N_2 + 1)(2N_3 + 1) = 2N + 1$ is the number of molecules in the crystal, and φ_m is the eigenfunction of a single molecule.

Suppose that the nth molecule absorbs a photon and makes a transition to an excited state. Then $\varphi_n \to \varphi_n^f$, where φ_n^f is the molecular wave–function of the excited state. The wave–function of the crystal will be a superposition

$$\Phi^f = (2N+1)^{-1/2} \times \sum_{n=-N}^{N} a^0_n \chi^f_n, \quad \chi^f_n = \varphi^f_n \prod_m \varphi_m. \tag{2}$$

Here $|a^0_n|^2$ is the statistical weight of the state in which the excitation is carried by the nth molecule. From the definition of an ideal crystal it follows that this quantity should be independent of n. The antisymmetrization of the wave–functions gives rise to very complicated formulas without significantly changing the results, and will for the sake of simplicity be omitted in our analysis. We substitute Eq. (2) into Eq. (1), multiply by χ^f_m and integrate over the internal variables of the molecular wave–functions. The result is

$$\sum_n{}' M^f_{nm} a^0_n - \varepsilon^f a^0_m = 0, \tag{3}$$

$$M^f_{nm} = \int \varphi_m \varphi^f_m \hat{V}^0_{nm} \varphi^f_n \varphi_n \, d\tau, \qquad (4)$$

where ϵ_f represents all the remaining terms, including the eigenvalue $\mathcal{E}$ (see Ref. 1, in which the same notations are used).

The matrix element M^f_{nm} determines the probability for transferring the excitation from the nth molecule to the mth. The formula shows that the greater the interaction energy, the more rapildy the exciton will migrate. Hence when we go from molecular to ionic crystals the migration velocity will in general increase. Further, the exciton will migrate with highest probability and therefore with highest velocity along those crystallographic directions in which the interaction is strongest.

If the interaction is due to a dipole–dipole force, then the transfer probability is $W \sim |M^f_{nm}|^2 \sim R^{-6}$, where R is the molecular separation. Any vibration of the crystal, even if the changes in the molecular separations are small, will produce a strong effect on the interaction, on the migration velocity, and finally on the line widths in the optical spectrum.

II. THE SEMI–INFINITE CRYSTAL

In an ideal crystal $|a^\circ_n|^2$ is independent of the index n, since all molecules in the crystal are equivalent. In a finite crystal the molecules at the surface are distinguished from molecules inside the crystal, and the values of $|a^\circ_n|^2$ will be different.

Suppose that a crystal is cut by a plane and the interaction between molecules on opposite sides of the plane ceases to exist. Between the molecules in each half of the crystal we suppose the interaction to be the same as in the infinite crystal. The lattice is supposed to be undisturbed, except for molecules close to the cutting plane where the interactions are different and some disturbance of the lattice may occur.

The equation for the semi–infinite crystal is

$$\Big(\sum_n \hat{H}_n + {}^1\!/_2 \sum_{nm}{}' \hat{V}_{nm} - \mathcal{E}\Big) \Phi = 0. \qquad (5)$$

The operator $\hat{V}_{nm}$ differs from $\hat{V}^\circ_{nm}$. Equation (5) may be written in the form

$$\Big(\sum_n \hat{H}_n + {}^1\!/_2 \sum_{nm}{}' \hat{V}^0_{nm} - {}^1\!/_2 \sum_{nm}{}' \hat{\Lambda}_{nm} - \mathcal{E}\Big) \Phi = 0, \qquad (6)$$

$$\sum_{nm}{}' \hat{\Lambda}_{nm} = \sum_{nm}{}' \hat{V}^0_{nm} - \sum_{nm}{}' \hat{V}_{mn}, \qquad (7)$$

where $\hat{\Lambda}_{nm}$ is a perturbation operator. If the nth and mth molecules are on opposite sides of the cutting plane, then by definition $\hat{V}_{nm} \equiv 0$. If the molecules are on the same side of the plane, then $\hat{V}_{nm} \equiv \hat{V}^\circ_{nm}$, and the perturbation operator is zero, except for molecules at the surface. Thus it is assumed that the perturbation does not penetrate deeply into the crystal.

We substitute Eq. (2) into Eq. (6), multiply by χ^f_m, and integrate over the internal molecular variables. The result is

$$\sum_n{}' a_n \int \varphi_m \varphi^f_m \hat{V}^0_{nm} \varphi_n \varphi^f_n d\tau + \sum_n{}' a_n \Big(\int \varphi_m \varphi^f_m \hat{V}_{nm} \varphi_n \varphi^f_n d\tau$$

$$- \int \varphi^f_m \varphi_m \hat{V}^0_{nm} \varphi^f_n \varphi_n d\tau \Big) - a_m \varepsilon^f_1 = 0, \qquad (8)$$

$$\sum_n{}' a_n M^f_{mn} - \sum_n{}' a_n \Lambda_{nm} - \varepsilon^f_1 a_m = 0,$$

where ϵ^f_1 denotes all the remaining terms, as before. The index n may be represented as a vector $n = n_1 \mathrm{i} + n_2 \mathrm{j} + n_3 \mathrm{k}$, where i, j, k are generators of the cubic lattice. The cutting plane is parallel to the plane of the vectors j, k and passes through the point $n_1 = 0$.

The problem can now be reduced to one dimension. Since the crystal remains periodic in the plane of the vectors j, k, we can write

$$a_n = a_{n_1 n_2 n_3} = a_{n_1} e^{i(\mathbf{n}_2 \mathbf{k}_2 + \mathbf{n}_3 \mathbf{k}_3)} = a_{n_1} e^{i \mathbf{n}_\tau \mathbf{k}_\tau},$$

$$\mathbf{k}_\tau = \sum_{i=2}^{3} (\pi / N_i)\, \mathbf{b}_i^{-1} \nu_i, \qquad -N_i \leqslant \nu_i \leqslant N_i,$$

$$\mathbf{n}_\tau = n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3,$$

Here b_i^{-1} is a vector of the reciprocal lattice, and b_2, b_3 are vectors of the physical lattice defining a plane cell.

This *ansatz* for the amplitudes means physically that we resolve the exciton wave into three directions and let these three component waves propagate independently of each other. The probability of finding the exciton at a given position (molecule) n_1, n_2, n_3, is then the product of the probabilities for finding it in the three planes passing through that position perpendicular to the lattice axes i, j, k.

We sum separately over thevariables n_2, n_3,

$$\sum_n{}' a_n M^f_{nm} = \sum_{n_1} a_{n_1} M^f_{n_1 m}(\mathbf{k}_\tau);$$

$$M_{n_1 m}(\mathbf{k}_\tau) = \sum_{n_2 n_3} e^{i\mathbf{n}_\tau \mathbf{k}_\tau} M^f_{n_1 m n_2 n_3}.$$

In the same way we write

$$\sum_n{}' a_n \Lambda_{nm} = \sum_{n_1} a_{n_1} \Lambda_{n_1 m}.$$

This summation means physically that we are considering the interaction of the mth molecule with a whole plane, say the $(m+g)$ th, of lattice–sites. The interaction of the mth molecule with the lattice plane in which it itself lies will not be disturbed by the cutting plane, and this interaction therefore does not affect the amplitude a_m or the energy level. Pictorially, we may say that the cutting of the crystal, with the assumptions which we have made, changes its properties only in the n_1 direction. Now n_1 may coincide with m.

The equation for a one–dimensional chain may be written

$$\sum_{n_1} a_{n_1} M^f_{n_1 m}(\mathbf{k}_\tau) - \sum_{n_1} a_{n_1} \Lambda_{n_1 m} - \varepsilon^f_1 a_m = 0. \tag{9}$$

Henceforth we shall write n instead of n_1. In matrix notation, the system of equations (9) becomes

$$(M - \Lambda - \varepsilon^f_1 E)\,\mathbf{a} = 0, \tag{10}$$

Here M is the matrix with elements M^f_{nm}, E is the unit matrix, Λ has elements Λ^f_{nm} and a is a column –matrix.

We consider the case in which the molecules interact not only with nearest neighbors but also weakly with next–nearest neighbors. Since we are now interested only in one half of the crystal (with $n_1 \geq 1$), the perturbation operator may be written

$$\frac{1}{2}\sum_{nm}(\Lambda_{nm}\delta_{n0}\delta_{m1} + \Lambda_{nm}\delta_{n1}\delta_{m0} + l\Lambda_{nm}\delta_{n2}\delta_{m1}$$
$$+ l\Lambda_{nm}\delta_{n1}\delta_{m2} + \Lambda_{nm}\delta_{n0}\delta_{m2} + \Lambda_{nm}\delta_{n2}\delta_{m0});$$

To avoid writing the factor 1/2, we suppose it henceforth included in the definition of each matrix element.

The first two terms represent the perturbation acting between the first layer of molecules of the left half of the crystal ($n \leq 0$) and the first layer of molecules of the right half. This perturbation must be assumed a little larger than $\hat{V}^{0}_{01}$, since in our model there is some interaction between the first layer of the right half and the second layer on the left. To avoid having additional terms in the operators, we suppose this perturbation of the first layer on the right by the second layer on the left to be already included at the beginning of the calculation. The magnitude of this perturbation will affect the numerical values but not the form of our results. The third and fourth terms represent the change in the interaction between the layers $n = 1$ and $n = 2$. The surface layers of the crystal will be compressed in the direction normal to the surface, and l is a measure of the magnitude of this effect. The fifth and sixth terms are the perturbation of the layer $n = 2$ by the layer $n = 0$. The δ_{ik} are Kronecker sybols.

III. THE PERTURBATION OPERATOR

We consider the one–dimensional perturbation operator as it was before the transition to matrix notation:

$$\hat{\Lambda} = \sum_{nm}{}' \hat{\Lambda}_{nm} = \sum_m \sum_n \hat{\Lambda}_{nm}.$$

First we transform it as follows:

$$\sum_n \hat{\Lambda}_{nm} = \sum_n (\hat{\Lambda}_{nm}\delta_{n0}\delta_{m1} \tag{11}$$
$$+ \hat{\Lambda}_{nm}\delta_{n1}\delta_{m0} + l\hat{\Lambda}_{nm}\delta_{n2}\delta_{m1}$$
$$+ l\hat{\Lambda}_{nm}\delta_{n1}\delta_{m2} + \hat{\Lambda}_{nm}\delta_{n0}\delta_{m_2} + \hat{\Lambda}_{nm}\delta_{n2}\delta_{m0} =$$
$$= \sum_n \sum_{i=1}^{2} (\alpha_{ni}\delta_{n0} + \beta_{ni}\delta_{n_1} + \varkappa_{ni}\delta_{n2})$$
$$\times (\gamma_{mi}\delta_{m0} + \mu_{mi}\delta_{m1} + \eta_{mi}\delta_{m2}).$$

The coefficients α, β, γ, etc. in Eq. (11) are determined by requiring that the final expression after expanding the brackets becomes identical with the preceding expression. In matrix notation the operator (11) becomes

$$\Lambda = \sum_{nm} \sum_{i=1}^{2} a_n L_n^i L_m^i; \tag{12}$$

$$L_n^i = \int \varphi_n \varphi_n^f (\alpha_{ni}\delta_{n0} + \beta_{ni}\delta_{n_1} + \varkappa_{ni}\delta_{n2})\, d\tau, \tag{13}$$

$$L_m^i = \int \varphi_m \varphi_m^f (\gamma_{mi}\delta_{m0} + \mu_{mi}\delta_{m_1} + \eta_{mi}\delta_{m2})\, d\tau.$$

Eq. (10) may be written

$$\mathbf{a} = (M - \varepsilon_1^f E)^{-1} \Lambda \mathbf{a}.$$

We express the vector Λ **a** as a superposition of eigenvectors of the unperturbed system, Λ **a** $= \Sigma\, \mathcal{L}_n\, \mathbf{a}_n^{\circ}$, the vectors $\mathbf{a}_n^{\circ}$ being orthogonal to each other. The orthogonality condition implies

$$\mathcal{L}_n = \mathbf{a}_n^0\, \Lambda \mathbf{a},$$

$$\mathcal{L}_0 = \sum_{i=1}^{2} a_0^0 (L_0^i L_1^i a_1 + L_0^i L_2^i a_2), \tag{14}$$

$$\mathcal{L}_1 = \sum_{i=1}^{2} a_1^0 (L_1^i L_0^i a_0 + L_1^i L_2^i a_2),$$

$$\mathcal{L}_2 = \sum_{i=1}^{2} a_2^0 (L_2^i L_0^i a_0 + L_2^i L_1^i a_1).$$

All the remaining coefficients are zero, since in the perturbation operator only three matrix elements are different from zero. We now let the operator $(M - \epsilon_1^f E)^{-1}$ act upon Λ **a** :

$$\mathbf{a} = (M - \varepsilon_1^f E)^{-1} \Lambda \mathbf{a} = \frac{\mathcal{L}_0}{\lambda_0 - \varepsilon_1^f}\, \mathbf{a}_0^0 + \frac{\mathcal{L}_1}{\lambda_1 - \varepsilon_1^f}\, \mathbf{a}_1^0 + \frac{\mathcal{L}_2}{\lambda_2 - \varepsilon_1^f}\, \mathbf{a}_2^0 \tag{15}$$

The coefficient $\mathcal{L}$ in the expansion of the vector Λ **a** in terms of the $\mathbf{a}_n^{\circ}$ are c–numbers, and therefore commute with the operator $(M - \epsilon_1^f E)^{-1}$. The vector $\mathbf{a}_n^{\circ}$ is an eigenvector of the unperturbed problem, i.e., it is an eigenvector of the operator M and λ_n is the corresponding eigenvalue.

The absolute square $|a_i|^2$, $-N \leq i \leq N$, of the ith component of the (in general infinite–dimensional) vector **a** in Eq. (10) is the probability of finding the exciton at the ith molecule. The vectors of the unperturbed and perturbed system are constructed in our model from the same basic states (the unit matrix is the same). From Eq. (15) it appears that the perturbed vector **a** has only 3 components different from zero, indicating that the exciton is localized close to the surface. In the expansion coefficients of the vector **a** [Eq. (15)] there appear the coefficients $\mathcal{L}_0$, $\mathcal{L}_1$, $\mathcal{L}_2$ defined by the expansion (14). To complete the solution of the problem we must calculate $\mathcal{L}_0$, $\mathcal{L}_1$, $\mathcal{L}_2$.

By operating with L_n^1 on Eq. (15), we obtain

$$L_0^1 a_0 + L_1^1 a_1 + L_2^1 a_2 = \frac{\mathcal{L}_0}{\lambda_0 - \varepsilon_1^f} L_0^1 a_0^0 + \frac{\mathcal{L}_1}{\lambda_1 - \varepsilon_1^f} L_1^1 a_1^0 + \frac{\mathcal{L}_2}{\lambda_2 - \varepsilon_1^f} L_2^1 a_2^0.$$

The operation of L_n^2 gives the analogous result

$$L_0^2 a_0 + L_1^2 a_1 + L_2^2 a_2 = \frac{\mathcal{L}_0}{\lambda_0 - \varepsilon_1^f} L_0^2 a_0^0 + \frac{\mathcal{L}_1}{\lambda_1 - \varepsilon_1^f} L_1^2 a_1^0 + \frac{\mathcal{L}_2}{\lambda_2 - \varepsilon_1^f} L_2^2 a_2^0.$$

These equations reduce to the form

$$a_1 (L_0^1 + L_1^1 - T_1 - T_2 - T_3 - T_3') + a_2 (L_2^1 - T_1' - T_2') = 0, \tag{16}$$

$$a_1 (L_0^2 + L_1^2 - T_1 - T_2 - T_3 - T_3') + a_2 (L_2^2 - T_1' - T_2') = 0;$$

$$T_1 = \frac{L_0^1 |a_0^0|^2}{\lambda_0 - \varepsilon_1^f} \sum_{i=1} L_0^i L_1^i, \qquad T_1' = \frac{L_0^1 |a_0^0|^2}{\lambda_0 - \varepsilon_1^f} \sum_{i=1}^{2} L_0^i L_2^i,$$

$$T_2 = \frac{L_1^1 |a_1^0|^2}{\lambda_1 - \varepsilon_1^f} \sum_{i=1}^{2} L_1^i L_0^i, \qquad T_2' = \frac{L_1^1 |a_1^0|^2}{\lambda_1 - \varepsilon_1^f} \sum_{i=1}^{2} L_1^i L_2^i,$$

$$T_3 = \frac{L_2^1 |a_2^0|^2}{\lambda_2 - \varepsilon_1^f} \sum_{i=1}^{2} L_2^i L_0^i, \qquad T_3' = \frac{L_2^1 |a_2^0|^2}{\lambda_2 - \varepsilon_1^f} \sum_{i=1}^{2} L_2^i L_1^i,$$

Using the condition that the two halves of the crystal are identical, we have put $|a_0| \equiv |a_1|$.

In order that Eq.(16) should have a non–zero solution, the determinant must vanish, and this gives a quadratic equation for ϵ_1^f.. When ϵ_1^f is known, the coefficients can be calculated from Eq. (15), and hence $\mathcal{L}_0$, $\mathcal{L}_1$, $\mathcal{L}_2$, and finally the eigenvalue $\mathcal{E}$, can be determined.

IV. CONCLUSIONS

The solution which we have found [Eq. (15) et seq.] extends only over the region of the crystal which is disturbed by the surface. We saw that $a_{n_1} = a_{n_1}\delta_{n_1 2} + a_{n_1 2}$, i.e., the amplitude is non-zero only at the surface. Such a solution, obtained by writing Eq. (10) in the form

$$a = (M - \varepsilon_1^f E)\,\Lambda a$$

exists only where the operator Λ is different from zero. Inside the crystal, where the surface has no effect on the molecular interactions, Davydov[1] has shown that solutions have the form of a plane exciton wave $e^{i(\mathbf{k}\mathbf{n}-\omega t)}$. Using Davydov's terminology, we may call the solution (15) a surface exciton wave, as opposed to a volume wave.

The surface exciton wave, which we call for brevity a surface exciton, occupies levels distinct from the levels of volume excitons. The number of lattice planes, into which the surface exciton penetrates, is fixed by the depth of penetration of the surface perturbation. The number of levels of a surface exciton in turn cannot exceed the number of lattice planes into which the exciton penetrates. Or if there are not one but α molecules in each plane cell $(b_2\, b_3)$, then each level splits into α bands. Each band finally has a continuous structure connected with the variation of the surface wave-vector k_τ of the exciton.

To observe a surface exciton spectroscopically, one must use a crystal with a large inter-molecular interaction. The heat of sublimation should be of the order of 10 kilo-calories per mole. The experiment must be done at the lowest possible temperature, and the specimen must have a large surface-to-volume ratio, (for example, a powder). Mosaic structure and microscopic cracks in a crystal should also cause surface excitons to appear at internal surfaces.

The method of calculation which we have used can also be successfully applied to problems connected with any kind of lattice irregularity in molecular crystals.

In conclusion, the author expresses his thanks to V. L. Levshin for his interest in the work, and to A. S. Davydov and I. V. Obreimov for valuable advice and criticism.

---

[1] A. S. Davydov, *Theory of Light Absorption in Molecular Crystals*, Ukrainian Academy of Sciences Press, Kiev, 1951).

[2] W. Ledermann, Proc. Roy. Soc. (London) A182, 362 (1944).

[3] I. M. Lifshitz and S. I. Pekar, Usp. Fiz. Nauk 6, 531 (1955).

[4] I. M. Lifshitz and L. N. Rosentsveig, J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 1013 (1948).

[5] I. M. Lifshitz, Dokl Akad. Nauk SSSR 58, 83 (1945).

[6] I. M. Lifshitz, J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 1016 (1947).

[7] I. M. Lifshitz, J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 1077 (1947).

Translated by F. J. Dyson
10