SOVIET PHYSICS JETP VOLUME 27, NUMBER 1 JULY, 1968

MULTIELECTRON THEORY OF EXCITONS IN SEMICONDUCTORS

V. P. MAKAROV

P. N. Lebedev Physics Institute, USSR Academy of Sciences

Submitted August 2, 1967

Zh. Eksp. Teor. Fiz. 54, 324–331 (January, 1968)

The Abrikosov, Gor'kov and Dzyaloshinskiĭ technique[10] is used to investigate the excited states of electrons in semiconductors. An equation for the exciton spectrum is derived. In the limiting case of large excitons radius the equation goes over into the Wannier-Mott equation with a static dielectric constant κ_0. Possible corrections to the Wannier-Mott equation are discussed as well as some experimental results pertaining to the exciton spectrum in cuprous oxide.

I. INTRODUCTION

It is well known that the long-wave edge of the spectrum of the main absorption in a number of semiconductors consists of a series of discrete lines connected with exciton production (see, for example, the views[1,2]). The greater part of the experimental results on exciton spectra in semiconductors can be successfully explained within the framework of the effective mass method (EMM). In the EMM the exciton is described in the simplest case by one equation of the Schrödinger type for two Coulomb interacting particles with effective masses m_e and m_h and effective charges $-e/\sqrt{\kappa}$ and $e/\sqrt{\kappa}$ respectively for the electron and the hole (κ is a certain effective dielectric constant of the crystal).

Since the dielectric constant κ is introduced purely phenomenologically in the EMM, the nature of κ, whether it is optical or static, can be established only outside the scope of the EMM (incidentally, different opinions concerning the meaning of κ are encountered in the literature[1-3]).

Investigations devoted to the determination of the effective electron-hole interaction usually follow one of two directions. A review of the work pertaining to one of these directions was presented by Knox[1], and we shall not dwell on it in detail here. We note only that, following Knox[1], all these approaches use a more or less artificial construction of the wave functions of the crystal, so that it remains unclear to what degree the results obtained in them can be directly applicable to excitons.

The authors of the papers dealing with the other direction start their calculations with the Schrödinger equation for all the crystal electrons, without introducing any charges that are "extraneous" with respect to the crystal. The excitons and the exciton spectrum are obtained respectively as excitations and the spectrum of the entire crystal. The fundamental work in this direction is the paper of Wannier[4], although in his paper, as well as in the later papers by others[5], the electron-hole interaction was obtained without screening.

Appreciable progress in the development of the entire trend was reached only recently, owing to the use of methods of quantum field theory. Kazarinov and Konstantinov[6] were the first to use a diagram technique to obtain the exciton spectrum. In their paper, however, the question of the dielectric constant κ was not resolved, and κ was introduced already in the initial Hamiltonian. Sham and Rice[7] solved fully the following problem of obtaining the EMM equation and κ from the total Hamiltonian of the crystal. In addition, they pointed out several possible corrections to the EMM.

An attempt to solve this problem was undertaken even earlier by Abe, Osaka and Morita[8]. However, even the original equation (3.6) in their paper seems to us incorrect. In fact, this equation should be integral not only in the wave vector, but also in the frequency (see Eq. (2.8) of our paper).

In addition to the papers indicated, there is one more devoted to the question of interest to us. This is the paper by Kubler[9], which essentially duplicates the calculations of Sham and Rice, and furthermore gives an incorrect formula for κ (it is sufficient to note that according to this formula $\kappa = 1$ for crystals of the Cu_2O type, in which the corresponding interband transition is forbidden).

In this paper we do the following: 1) we derive the EMM equation for the excitons by a method different from that of Sham and Rice[7]; 2) we derive an equation which is more general than the usual EMM equation, and from which the latter is obtained in the limiting case of large-radius excitons; 3) we present formulas for different corrections to EMM, and these corrections are discussed together with certain experimental results.

We use the technique of Abrikosov, Gor'kov, and Dzyaloshinskiĭ[10]. In the formulation of the problem which follow essentially Sec. 19 of their book[10]. In the entire paper, with the exception of those places where numerical estimates are given, we use a system of units in which $\hbar = 1$.

2. EQUATION FOR THE TWO-PARTICLE GREEN'S FUNCTION

In this paper we use the simplest model of a crystal. We assume that a conduction band c and the valence band v, with which the exciton is connected, have at small values of the quasimomentum $|p| \ll 1/d$ (d—lattice constant) quadratic dispersion laws with isotropic effective masses

$$\varepsilon_c(\mathbf{p}) = \varepsilon_g + p^2/2m_e, \qquad \varepsilon_v(\mathbf{p}) = -p^2/2m_h. \tag{2.1}$$

(ϵ_g is the width of the forbidden band). We note, however, that the distortion of the exciton spectrum due to the anisotropy of the masses, band degeneracy, spin-orbit interaction, or the influence of other bands can be investigated within the framework of the EMM itself[11,12].

Assume that at the instant of time t_0 the crystal is in an excited state described in the interaction representation by the vector

$$|\Phi_1(t_0)\rangle = \sum_{\mathbf{p}} \varphi_{n\mathbf{k}}(\mathbf{p}) a^{+}_{c\mathbf{p}+\mathbf{k}}(t_0) a_{v\mathbf{p}}(t_0) |\Phi_0(t_0)\rangle. \tag{2.2}$$

Here $|\Phi_0(t)\rangle$ is the vector of the ground state of the crystal in the interaction representation, $\mathbf{k}$ is the excitation quasimomentum, n is the set of the remaining quantum numbers characterizing the excited state, $\varphi_{n\mathbf{k}}(\mathbf{p})$ are the amplitudes to be determined, and $a^{+}(t)$ and $a(t)$ are the creation and annihilation operators, also in the interaction representation. The values of $\mathbf{p}$ and $\mathbf{k}$ are bounded by the Brillouin zone.

At the instant of time $t > t_0$ the crystal is in a certain state Φ_2. The amplitude of the probability of the state Φ_1 at the instant of time t is obtained in the usual manner (see Sec. 19 of[10]). It is determined by the following formulas:

$$\langle\Phi_1(t)|\Phi_2(t)\rangle = -\sum_{\mathbf{p}_1\mathbf{p}_2} \varphi^{*}_{n\mathbf{k}}(\mathbf{p}_2)\varphi_{n\mathbf{k}}(\mathbf{p}_1) \int F(\mathbf{p}_1, \mathbf{p}_2; k) e^{-i\omega(t-t_0)} \frac{d\omega}{2\pi} \tag{2.3}$$

$$F(\mathbf{p}_1, \mathbf{p}_2; k) = \int G^{\mathrm{II}}_{cv;\, vc}(p_2 + k, p_1; p_2, p_1 + k) e^{i(\omega_1\tau_1+\omega_2\tau_2)} \frac{d\omega_1\, d\omega_2}{(2\pi)^2}, \quad \tau_1, \tau_2 \to +0, \tag{2.4}$$

$$G^{\mathrm{II}}_{cv;\, vc}(p_2 + k, p_1; p_2, p_1 + k) = -G_{cc}(p_2 + k) G_{vv}(p_1) \cdot 2\pi\delta(\omega_1 - \omega_2)\delta_{\mathbf{p}_1\mathbf{p}_2} + iG_{c\lambda}(p_2 + k) G_{v\mu}(p_1) \Gamma_{\lambda\mu;\, \nu\sigma}(p_2 + k, p_1; p_2, p_1 + k) G_{\nu v}(p_2) G_{\sigma c}(p_1 + k). \tag{2.5}$$

To abbreviate the notation, we have introduced here the 4-vectors $p_1 \equiv \mathbf{p}_1, \omega_1$, $p_2 \equiv \mathbf{p}_2, \omega_2$, and $k \equiv \mathbf{k}, \omega$; we have also dropped the symbols c and v from the function F. Summation over the repeated Greek indices which number the energy bands is implied (in particular cases λ, μ, ν, or σ can coincide with c or v). In the right side of (2.5), which describes the two-particle Green's function G^{II} in terms of the vertex part Γ, we have left out an inessential term $G_{\mathrm{cv}}(p_2) G_{\mathrm{vc}}(p_1) \cdot 2\pi\delta(\omega)\delta_{\mathrm{k}0}$. In deriving (2.5) we also used the fact that the Green's function G of the electron in the crystal is diagonal in the quasimomentum $\mathbf{p}$, this being a consequence of the translational symmetry of the lattice.

The spectrum of the two-particle crystal excitations that have a specified quasimomentum $\mathbf{k}$ is determined by the poles of the function F, which lie in the lower half-plane of the complex variable ω (see Sec. 19 of[10]). To determine the function F, we first derive an equation that must be satisfied by the two-particle Green's function G^{II}. In the zeroth approximation, when $\Gamma = 0$ and $G_{\mathrm{V}}(p_1 \equiv G_{\mathrm{VV}}(p_1) = G^{(0)}_{\mathrm{V}}(p_1)$ and also $G_{\mathrm{C}}(p_2 + k) \equiv G_{\mathrm{CC}}(p_2 + k) = G^{(0)}_{\mathrm{C}}(p_2 + k)$, where the Green's functions of the free particles[10] are

$$G_c^{(0)-1}(p_2 + k) = \omega_2 + \omega - \varepsilon_c(\mathbf{p}_2 + \mathbf{k}) + i\delta,$$
$$G_v^{(0)-1}(\mathbf{p}_1) = \omega_1 - \varepsilon_v(\mathbf{p}_1) - i\delta, \quad \delta \to +0, \tag{2.6}$$

we get

$$F^{(0)}(\mathbf{p}_1, \mathbf{p}_2; k) = -\frac{i}{\omega - \varepsilon_c(\mathbf{p}_2 + \mathbf{k}) + \varepsilon_v(\mathbf{p}_2) + i\delta}\delta_{\mathbf{p}_1\mathbf{p}_2} \tag{2.7}$$

In this approximation the sought spectrum coincides, as it should, with the spectrum of the free electron-hole pair: $\omega = \epsilon_{\mathrm{c}}(\mathbf{p} + \mathbf{k}) - \epsilon_{\mathrm{v}}(\mathbf{p})$.

The experimentally observed exciton spectrum corresponds to excitation energies $\omega = \epsilon_{\mathrm{g}} - |\epsilon|$, such that $|\epsilon| \ll \epsilon_{\mathrm{g}}$. This makes it possible to regard the exciton levels in the semiconductors as shallow levels, and the ratio $|\epsilon|/\epsilon_{\mathrm{g}} \ll 1$ as the small parameter in the exciton theory.

As the zeroth approximation we choose the Hartree-Fock approximation. Then, out of the four diagrams corresponding to the first-order corrections to the function G^{II}, it is necessary to take into account only two diagrams for Γ. The contribution from the other two diagrams (see Fig. 16 of[10]) vanishes in any order[13].

A simple analysis shows that out of all the second-order diagrams for the vertex part Γ (see Fig. 57 of[10]), one diagram is singled out, and in it the pole of the two Green's functions $G^{(0)}_{\mathrm{C}}(p_3 + k)$ and $G^{0}_{\mathrm{V}}(p_3)$ in the frequency region of interest to us $\omega \approx \epsilon_{\mathrm{g}}$ come closer together (the integration is carried out with respect to ω_3). Denoting by $\langle \mathrm{cp}_2 + \mathrm{k},\ \mathrm{vp}_1 | \overline{\mathrm{U}} | \mathrm{vp}_2,\ \mathrm{cp}_1 + \mathrm{k}\rangle$ the aggregate of all the diagrams for Γ which do not contain "singular" elements, that is, lines $G^{(0)}_{\mathrm{C}}(p_3 + k) G^{(0)}_{\mathrm{V}}(p_3)$, we can write for $\Gamma_{\mathrm{cv;vc}}(p_2 + k, p_1; p_2, p_1 + k)$ an integral equation analogous to (18.3) of[10]. Leaving out this equation, we write down immediately the equation for the function G^{II}, which is connected with Γ by formula (2.5). This equation is

$$G^{\mathrm{II}}_{cv;\, vc}(p_2 + k, p_1; p_2, p_1 + k) = -G_c^{(0)}(p_2 + k) G_v^{(0)}(p_2) \times\Big\{2\pi\delta(\omega_1 - \omega_2)\delta_{\mathbf{p}_1\mathbf{p}_2} + i\sum_{\mathbf{p}_3}\int \langle cp_2 + k, vp_3|\overline{U}|vp_2, cp_3 + k\rangle \times G^{\mathrm{II}}_{cv;\, vc}(p_3 + k, p_1; p_3, p_1 + k)\frac{d\omega_3}{2\pi}\Big\}. \tag{2.8}$$

The right side of this equation should contain, generally speaking, the exact Green's functions G, and not $G^{(0)}$. It can be shown, however, that the difference between them, which obviously appears only in second order in the interaction between the electrons, leads to negligibly small corrections to the exciton energy.

In the next section we shall obtain on the basis of (2.8) an equation for the function F and find its solution.

3. DERIVATION OF THE EQUATION FOR THE EXCITONS

We first obtain an expression for $\overline{\mathrm{U}}$. The form of $\overline{\mathrm{U}}$ in the first order in the interaction is obvious;

$$\langle cp_2 + k, vp_3|\overline{U}|vp_2, cp_3 + k\rangle = -\langle c\mathbf{p}_2 + \mathbf{k}, v\mathbf{p}_3|U|c\mathbf{p}_3 + \mathbf{k}, v\mathbf{p}_2\rangle + \langle c\mathbf{p}_2 + \mathbf{k}, v\mathbf{p}_3|U|v\mathbf{p}_2, c\mathbf{p}_3 + \mathbf{k}\rangle, \tag{3.1}$$

where, for example, the second term on the right is the matrix element of the energy of interaction between the electrons $U = e_2/|\mathbf{r}_1 - \mathbf{r}_2|$ corresponding to a transition between the Bloch states $\mathrm{cp}_2 + \mathrm{k} \to \mathrm{vp}_2$ and $\mathrm{vp}_3 \to \mathrm{cp}_3 + \mathrm{k}$. Sometimes the matrix elements for U are best written in the form of a series in the reciprocal-lattice vectors[6].

We defer a discussion of the second term in the right side of (3.1) to the next section. An approximation of $\overline{\mathrm{U}}$ by the first term in the right side of (3.1) corresponds, obviously, to neglect of the crystal polarization. At small quasimomentum transfers $|\mathbf{p}_3 - \mathbf{p}_2|$ this matrix element is equal to $4\pi e^2/V|\mathbf{p}_3 - \mathbf{p}_2|$, where V is the volume of the crystal. In this case diagrams of higher order become important and we must sum a chain of diagrams, similar to that shown in Fig. 60 of[10]. As a result of this summation we obtain

$$\langle cp_2 + k, vp_3|\overline{U}|vp_2, cp_3 + k\rangle = -\frac{\langle c\mathbf{p}_2 + \mathbf{k}, v\mathbf{p}_3|U|c\mathbf{p}_3 + \mathbf{k}, v\mathbf{p}_2\rangle}{\varkappa(\mathbf{p}_2 - \mathbf{p}_3, \omega_2 - \omega_3)}, \quad (3.2)$$

where $\kappa(q, \omega_q)$ represents the dielectric constant of the semiconductor (see formula (5.42) in[14]).

The physical meaning of formulas (2.8) and (3.2) is exceedingly lucid; the electron-hole pair producing the exciton polarizes the crystal, which in turn screens the electron-hole interaction; the polarization, together with the screening, depends on which exciton state is excited.

In the equation for G^{II}, which is obtained by substituting (3.2) in the right side of (2.8), we can neglect the frequency dispersion of the dielectric constant $\kappa(q, \omega_q)$, putting in κ $\omega_q = 0$, as follows from (2.8) and (3.2) and from the condition $\omega \approx \epsilon_q$. The corresponding equation for the function F will then take the form

$$[\varepsilon_c(\mathbf{p}_2 + \mathbf{k}) - \varepsilon_v(\mathbf{p}_2) - \omega - i\delta]F(\mathbf{p}_1, \mathbf{p}_2; k)$$
$$- \sum_{\mathbf{q}} \frac{\langle c\mathbf{p}_2 + \mathbf{k}, v\mathbf{p}_2 + \mathbf{q}|U|c\mathbf{p}_2 + \mathbf{k} + \mathbf{q}, v\mathbf{p}_2\rangle}{\varkappa(\mathbf{q})} F(\mathbf{p}_1, \mathbf{p}_2 + \mathbf{q}; k) = i\delta_{\mathbf{p}_1\mathbf{p}_2}, \quad (3.3)$$

where $\kappa(\mathbf{q}) \equiv \kappa(\mathbf{q}, 0)$ is the static dielectric constant, which takes into account the spatial dispersion.

The solution of (3.3) can be expressed in terms of the amplitudes $\varphi_{nk}(p)$ that enter in (2.2) in the following manner:

$$F(\mathbf{p}_1, \mathbf{p}_2; k) = -i \sum_n \frac{\overset{*}{\varphi}_{n\mathbf{k}}(\mathbf{p}_1)\varphi_{n\mathbf{k}}(\mathbf{p}_2)}{\omega - \varepsilon_{n\mathbf{k}} + i\delta}. \quad (3.4)$$

The functions $\varphi_{nk}(p)$, which are assumed to form a complete system, are the solutions of the equation

$$[\varepsilon_c(\mathbf{p} + \mathbf{k}) - \varepsilon_v(\mathbf{p})]\varphi_{n\mathbf{k}}(\mathbf{p})$$
$$- \sum_{\mathbf{q}} \frac{\langle c\mathbf{p}+\mathbf{k}, v\mathbf{p} + \mathbf{q}|U|c\mathbf{p}+\mathbf{k} + \mathbf{q}, v\mathbf{p}\rangle}{\varkappa(\mathbf{q})} \varphi_{n\mathbf{k}}(\mathbf{p} + \mathbf{q}) = \varepsilon_{n\mathbf{k}}\varphi_{n\mathbf{k}}(\mathbf{p}). \quad (3.5)$$

We note that it follows from (2.3) and (3.4) that the probability amplitude of the excited state (2.2) oscillates in time at a frequency ϵ_{nk}, as should be the case for a stationary state with such an energy.

Equation (3.5) is valid for excitons with low binding energies. If, in addition, the amplitudes $\varphi_{nk}(p)$ differ noticeably from zero only in the region $|p| \ll 1/d$ and the excitation quasimomentum $|k| \ll 1/d$, then (3.5) simplifies appreciably. The summation over q in the left side of the equation can in this case be extended to all of q-space, after which it is possible to go over from summation to integration. Further, the dispersion of $\epsilon_c(p)$ and $\epsilon_v(p)$ for all p can be regarded as quadratic (Eq. (2.1)), and the matrix element $\langle \ldots |U| \ldots \rangle$ in (3.5) can be replaced by $4\pi e^2/Vq^2$.

After a few simple transformations we obtain the following result:

$$\varphi_{n\mathbf{k}}(\mathbf{p}) = \chi_n\left(\mathbf{p} + \frac{m_h}{M}\mathbf{k}\right), \quad \varepsilon_{n\mathbf{k}} = \varepsilon_g + \frac{k^2}{2M} + \varepsilon_n, \quad \varepsilon_n = -\frac{m^* e^4}{2\varkappa_0^2 n^2},$$
$$m^* = \frac{m_e m_h}{M}, \quad M = m_e + m_h, \quad (3.6)$$

where the functions $\chi_n(p)$, $n = 1, 2, \ldots$, are the solutions of the hydrogen-like equation in the momentum representation

$$\frac{p^2}{2m^*}\chi_n(\mathbf{p}) - \frac{e^2}{2\pi^2\varkappa_0} \int \frac{\chi_n(\mathbf{p} + \mathbf{q})}{q^2} d\mathbf{q} = \varepsilon_n\chi_n(\mathbf{p}). \quad (3.7)$$

By κ_0 we denote here the static macroscopic dielectric constant of the crystal, that is, $\kappa(q)$ as $q \to 0$[14].

Equation (3.7) is the EMM equation describing the relative motion of the electron and hole in the exciton. It is also called the Wannier-Mott equation.

4. CORRECTIONS TO THE EMM

The simple calculations which we shall now present show that, out of all the diagrams discarded in the derivation of (3.5), only the one corresponding to the second term in the right side of (3.1) leads to an appreciable correction to the exciton energy. (We recall that we are considering only excitons with low binding energy $|\epsilon| \ll \epsilon_g$). Physically this correction takes into account the change of the exchange energy of the electrons upon excitation of the crystal.

Allowance for the second term in the right side of (3.1) leads, as can be readily verified, to the appearance in the left side of (3.5) of an additional term

$$\sum_{\mathbf{q}} \langle c\mathbf{p} + \mathbf{k}, v\mathbf{p} + \mathbf{q}|U|v\mathbf{p}, c\mathbf{p} + \mathbf{k} + \mathbf{q}\rangle \varphi_{n\mathbf{k}}(\mathbf{p} + \mathbf{q}). \quad (4.1)$$

We confine ourselves to the calculation of the exchange correction to the large-radius exciton levels with small k; the latter are of particular interest in optics. In this case the matrix element under the summation sign in (4.1) can be calculated by the kp perturbation method well known from semiconductor theory (see, for example,[3]). As a result we get,

$$\langle c\mathbf{p} + \mathbf{k}, v\mathbf{p} + \mathbf{q}|U|v\mathbf{p}, c\mathbf{p} + \mathbf{k} + \mathbf{q}\rangle = 4\pi e^2|p_{cv}|^2/Vm^2\varepsilon_g^2, \quad (4.2)$$

where p_{cv} is the matrix element of one of the momentum components of the interband transition in the center of the Brillouin zone. Regarding the corresponding additional term in (3.7) as a perturbation, we obtain in the first order of perturbation theory

$$\Delta\varepsilon_{nex}^{(1)} = \frac{4\pi e^2|p_{cv}|^2}{m^2\varepsilon_g^2}|\psi_n(0)|^2, \quad (4.3)$$

where $\psi_n(r)$ is a hydrogenlike wave function in the coordinate representation.

The exchange correction (4.3) differs from zero only for s-excitons, whose binding energy it lowers. The latter circumstance follows, incidentally, also from general considerations. This lifts partially the momentum degeneracy.

If $a = \kappa_0/m^*e^2$ is the Bohr radius of the exciton, then $|\psi_n(0)|^2 = (\pi n^3 a^3)^{-1}$[15]. Therefore $\Delta\epsilon_{nex}^{(1)} \sim 1/n^3$, whereas $\epsilon_n \sim 1/n^2$. Consequently, the s-excitons cannot produce a hydrogenlike spectrum, provided, of course, the quantity (4.3) cannot be neglected in comparison with ϵ_n. As to the quantity

$$\frac{\Delta\varepsilon_{nex}^{(1)}}{|\varepsilon_n|} = \frac{32\varkappa_0^3 n^3|p_{cv}|^2}{m^2e^4}\left|\frac{\varepsilon_n}{\varepsilon_g}\right|^2 \quad (4.4)$$

it can be asserted in general that it cannot be neglected. Thus, for example, in a CdS crystal, where $\kappa_0 = 9.3$, $|\epsilon_1| = 0.028$ eV, $\epsilon_q = 2.58$ eV, and the oscillator strength for the transition to the lower exciton state is

$f_1 = 2.6 \times 10^{-3}$ [16], the quantity (4.4) is equal to 0.2. In Ge it is apparently of the same order[8]. In the second order of perturbation theory, we would obtain the value $\Delta\epsilon_{nex}^{(2)}/\epsilon_1 \approx (\Delta\epsilon_{nex}^{(1)}/2\epsilon_1)^2$, which also differs from zero only for the s-states. In the case of CdS its value is 0.01.

As is well known[1,11,13], the optical transitions in the s-exciton states are forbidden in the dipole approximation if the interband transition is forbidden in this approximation, that is, $p_{cv} = 0$. The dipole transitions are allowed in the p-states for which the exchange correction (4.3) vanishes (as well as for all states if $p_{cv} = 0$). Consequently, a hydrogenlike exciton absorption (or reflection) spectrum should be observed more readily in those semiconductors in which the corresponding interband transition is forbidden. In addition, the crystals should, of course, be cubic in order that the dielectric constant κ_0 be a scalar, and should also have c- and v-bands that would conserve the quadratic dispersion law (2.1) in a region of the Brillouin zone with linear dimensions of the order of the reciprocal of the Bohr radius a of the exciton.

Such a crystal is cuprous oxide Cu_2O, in which several exciton series were observed[1,2,17]. We consider here only one of them, the so called "yellow" series. It has been shown experimentally[2] that nine out of the ten identified exciton levels of this series are well described by formula (3.6) with $n = 2, 3, \ldots 10$. At the same time, the binding energy of the 1s-exciton, $|\epsilon_1| \approx 0.14$ eV, is larger by approximately 0.04 eV than the value that follows from formula (3.6) with $n = 1$.

This circumstance is a reflection of the fact that the 1s-exciton in Cu_2O is not a large-radius exciton. Indeed, assuming $\kappa_0 = 9$ [17] and using the experimental value of the exciton Rydberg constant 0.097 eV, we obtain for the reduced mass the value $m^* \approx 0.6$ m and for the Bohr radius of the exciton the value $a \approx 8 \times 10^{-8}$ cm. The lattice constant of Cu_2O is $d \approx 4 \times 10^{-8}$ cm, so that the ratio $d/a \approx 0.5$, and the inequality $a \gg d$ is not satisfied, i.e., the EMM equation (3.7) is not valid for the 1s-exciton. On the other hand, the ratio of the binding energy of the 1s-exciton $|\epsilon_1| \approx 0.14$ eV to the forbidden band width $\epsilon_q \approx 2.2$ ev is $|\epsilon_1|/\epsilon_q \approx 0.06 \ll 1$. Consequently, the validity of Eq. (3.5) is subject to no doubt in this case.

The exact solution of (3.5), in any case, calls for knowledge of the Bloch functions and of the function $\kappa(q)$. We therefore confine ourselves to an approximate solution of this equation.

Following Knox[1], we assume that the quadratic dispersion law (3.1) remains valid also for the 1s-exciton. Then, obviously, the matrix element in (3.5) can as before assumed equal to $4\pi e^2/Vq^2$. At small $q(q < 1/d)$ the function $\kappa(q)$ can be represented in the form of a series in powers of q (more accurately in powers of qd), and we can confine ourselves here to the first two terms of the expansion. Since $\kappa(\mathbf{q})$ is an even function of $\mathbf{q}$ and is furthermore a decreasing function (at any rate for small q), we can assume that

$$\varkappa(\mathbf{q}) = \varkappa_0 - \alpha(qd)^2, \tag{4.5}$$

where α is a positive constant of the order of unity. Regarding the additional term which appears in this case in (3.6) as a perturbation, we obtain in the first order of perturbation theory

$$\Delta\varepsilon_{nq}^{(1)} = -\frac{4\pi e^2 \alpha d^2}{\varkappa_0{}^2} |\psi_n(0)|^2. \tag{4.6}$$

Substituting here $|\psi_n(0)|^2$, we get for the 1s-exciton

$$\frac{\Delta\varepsilon_{1q}^{(1)}}{\varepsilon_1} = \frac{8\alpha}{\varkappa_0}\left(\frac{d}{a}\right)^2 \approx 0.2\alpha \tag{4.7}$$

The second-order correction can be neglected since $\Delta\epsilon_{1q}^{(2)}/\epsilon_1 \approx 0.01\,\alpha^2 \ll \Delta\epsilon_{1q}^{(1)}/\epsilon_1$. When $\alpha = 1.5$, the value $\Delta\epsilon_{1q}^{(1)}/\epsilon_1 \approx 0.3$ calculated from formula (4.7) coincides with the corresponding experimental value[1,2,17].

It should be noted that similar corrections will be necessary also for other levels with $n > 1$, since $\Delta\epsilon_{nq}^{(1)}/\epsilon_n \sim 1/n$. But these corrections pertain, as follows from (4.6), only to the s-states and therefore are not connected at all with the dipole exciton lines of the "yellow" series.

In conclusion, let us stop to discuss the allowance for the frequency dispersion of the dielectric constant $\kappa(\mathbf{q}, \omega)$. From the very derivation of (3.5)–(3.7) it is sufficiently clear that the correction to the exciton energy due to allowance for the frequency dispersion is small compared with the corrections discussed above. In order to verify this, it is necessary to turn to Eq. (2.8) for the two-particle Green's function, in which $\bar{U}$ is determined by formula (3.2). An estimate of the corresponding correction can be made in analogy with (4.5)–(4.7). Accurate to a numerical coefficient, the correction to the exciton levels for the frequency dispersion of the dielectric constant κ is equal to $|\Delta\epsilon_{n\omega}^{(1)}/\epsilon_n| \approx (\epsilon_n/\epsilon_q)^2\kappa_0^{-1}$. This quantity is at least two orders of magnitude smaller than the correction (4.7) for the spatial dispersion of κ, and three orders smaller than the exchange correction (4.4) in CdS.

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Translated by J. G. Adashko
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