

SURFACE EXCITONS OF ELECTRON-HOLE TYPE AND COLLECTIVE PHENOMENA ASSOCIATED WITH THEM

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We discuss the question of surface excitons of the electron-hole type (their binding energy is calculated in the "macroscopic" approximation). Mention is made of a number of possibilities that arise when the concentration of the surface excitons increases.

The problem of surface levels as applied to metals and semiconductors has been under discussion since 1932 [1], but there are still many obscure aspects from the theoretical and particularly from the experimental point of view [2]. At the same time, an increased interest in surface levels is already observed and one can expect even more in the nearest future, owing to the development of adequate experimental methods. We wish to call attention here to the possible existence of surface excitons of the electron-hole type (i.e., excitons of the Wannier-Mott type (this circumstance was already pointed out in [3, 4], but the question was not discussed in detail). In the simplest case of isotropic parabolic bands, the binding energy of a surface exciton is determined from the two-dimensional Schrodinger equation

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x, y) \right] \psi(x, y) = E \psi(x, y). \quad (1)$$

Here  $m^{-1} = m_e^{-1} + m_h^{-1}$ , where  $m_e$  and  $m_h$  are the effective masses of the electrons and holes in the surface bands. This equation is exact, as is the equation for three-dimensional Wannier-Mott excitons (see, e.g., [5]). The spatial inhomogeneity of the problem is taken into account when determining the type of the operator of the electron-hole interaction  $V(x, y)$ . Let the region near the boundary in which the surface states are localized have a thickness of the order of  $b$ . When  $b \gg a$  ( $a$  is of the order of the lattice constant),  $V(x, y)$  can be determined by using a macroscopic image method, for in this case the image is located far enough from the separation boundary. Let the dielectric constant of the medium be  $\epsilon_1$  at  $z < 0$  and  $\epsilon_2$  at  $z > 0$ . The energy  $U(\rho, z_e, z_h)$  of the electrostatic interaction of an electron and hole located at points with coordinates  $x_e, y_e, z_e$  and  $x_h, y_h, z_h$  is equal to  $-(e^2/\epsilon_2)[1/R + \alpha/R']$  if  $z_e > 0$  and  $z_h > 0$  to  $-(e^2/\epsilon_1)[1/R - \alpha/R']$  if  $z_e < 0$  and  $z_h < 0$ , and to  $-2e^2/(\epsilon_1 + \epsilon_2)$  if  $z_e z_h < 0$ . Here  $\alpha = (\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$ ,  $\rho = [(x_e - x_h)^2 + (y_e - y_h)^2]^{1/2}$ ,  $R = [\rho^2 + (z_e - z_h)^2]^{1/2}$ , and  $R' = [\rho^2 + (z_e + z_h)^2]^{1/2}$ . At sufficiently large distance between the electron and the hole, the operator  $V(x, y)$  is given by the diagonal matrix element (see [5])

$$\int dx_e dy_e dz_e dx_h dy_h dz_h |a_{00}(x_h, y_h, z_h)|^2 |b_{xy}(x_e, y_e, z_e)|^2 U(\rho, z_e, z_h), \quad (2)$$

where  $a_{00}$  and  $b_{xy}$  are the wave function of the surface bands in the Wannier

representation. If  $b \ll r_0$ , where  $r_0$  is the exciton "radius" (see below), then, accurate to terms of order  $(b/r_0)^2$ , the operator is  $V(x, y) = -2e^2/(\epsilon_1 + \epsilon_2)r$ , where  $r = [x^2 + y^2]^{1/2}$ . Of course, such a result is obtained immediately if we use the expression for  $U(\rho, z_e, z_h)$  at  $\rho = r$  and  $z_e = z_h = 0$  (by the same token, such a procedure becomes justified).

For the binding energy and the wave function of the ground state  $n = 0$  we obtain from (1) the expressions

$$E_n = - \frac{2me^4}{\hbar^2(\epsilon_1 + \epsilon_2)^2} \left( n + \frac{1}{2} \right)^{-2}, \quad n = 0, 1, 2, \dots \quad (3)$$

$$\psi_0(r) = \left( \frac{\pi r_0^2}{2} \right)^{-1/2} \exp(-r/r_0), \quad r_0 = \frac{\hbar^2(\epsilon_1 + \epsilon_2)}{4me^2}.$$

At the seemingly realistic values  $m \sim (10^{-1} - 10^{-2})m_0$  and  $\epsilon_1 + \epsilon_2 \sim 10$ , we have  $E_0 \sim (0.1 - 1) \text{ eV}$  and  $r_0 \sim (10 - 150) \text{ \AA}$ , where  $m_0$  is the mass of the free electron.

The values of  $\epsilon_1 + \epsilon_2$  should be taken for the frequencies  $\omega \lesssim E_0/\hbar \sim 10^{14}$ , which for real materials can correspond fully to the use of the low-frequency values of  $\epsilon_1 + \epsilon_2$ . Even under conditions when the assumptions made (the condition  $b \gg a$  and others) are not well satisfied, formulas (3) can probably still serve for estimates (the same can be said with respect to the boundary with the vacuum, when  $\epsilon_1 = 1$ ).

The surface-exciton spectrum can be investigated, for example, by measuring the energy lost by particles crossing the interface, by determining the absorption of light, or by the Raman-scattering method [6]. By one method or another, it is possible, of course, also to "pump up" surface excitons.

When the surface-exciton concentration is increased, they should form biexcitons (in the surface, i.e., two-dimensional case, as is well known, a biexciton level will exist already at an arbitrary weak attraction between the excitons). At sufficiently low temperatures and sufficiently high concentrations  $n$ , particularly in the region  $nr_0^2 \geq 1$ , the exciton and biexciton gases becomes collectivized, and different possibilities exist [7]. It can be assumed that, just as in the three-dimensional case, there can be realized in principle conditions corresponding to Bose condensation<sup>1)</sup>, formation of an exciton "liquid" of the dielectric and metallic type, appearance of "drops," etc. To be sure, the ordinary long-range order of superfluid or superconducting type is impossible in two-dimensional systems. For finite (but still macroscopic) surfaces, however, an ordering close to the usual one is possible (with a critical temperature  $T_c$  that decreases logarithmically with increasing surface [10]). In addition, superfluidity and superconductivity or their analogs can apparently appear even for infinite surfaces [10 - 12]. It is important here that at  $r_0 \geq 10^{-6} \text{ cm}$  the high concentration (the condition  $nr_0^2 \sim 1$ ) is reached already at  $n \lesssim 10^{12} \text{ cm}^{-2}$ .

Arguments analogous to those presented above can be advanced also with respect to the one-dimensional case, which can be of interest when applied to the edges of crystal faces, to dislocations, to "whiskers," and to polymers. In this

<sup>1)</sup> Bose condensation of excitons of certain types constitutes formation of a macroscopic electromagnetic wave with specified phase (see [8]). It is clear even from this that Bose condensation of surface excitons is possible, since it corresponds to the appearance of surface electromagnetic waves (see [9]).

case, obviously, the exciton system is dense already at  $nr_0 \sim 1$ , corresponding to a concentration  $n \lesssim 10^6$  ( $r_0 \gtrsim 10^{-6}$  cm).

In addition to exciton formation, surface superconductivity (more accurately, quasisuperconductivity; see above), which results in the equilibrium case from attraction between electrons (see [10, 13]), is worthy of attention. Under non-equilibrium conditions (in the case of inverted population), the superconductivity should arise, to the contrary, when there is repulsion between electrons or holes [14].

Thus, there is indeed a large circle of interesting problems (including also the actions of the magnetic field, allowance for anisotropy, and other factors not mentioned above), which can serve as the subject of various theoretical and experimental researches.

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#### EFFECTS OF THE OPTICAL "NUTATION" TYPE IN MULTIPLE PHOTON ECHO

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We consider theoretically the propagation of two ultrashort pulses (USP) of light in a dense resonant medium.

1. Coherent interaction of powerful optical pulses with a resonant medium leads to a large number of nonstationary nonlinear-optical effects [1 - 3]. One presently well-known effect is photon echo [1], where in the action of two optical pulses separated by a time interval  $\tau$  produces in a medium a coherent quantum state that leads to the emission of a third light pulse at the instant  $2\tau$ . Equally well established is the phenomenon of optical nutation [2], where a rectangular optical pulse produces in a medium periodic variation of the