Exciton localization on defects that produce resonant energy levels

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(Submitted 1 July 1982)
Zh. Eksp. Teor. Fiz. **84**, 679–685 (February 1983)

The localization of electrons on defects that produce resonant (virtual) energy levels near the boundaries of the forbidden band of semiconducting crystals is considered. It is shown that such a defect, without binding each carrier separately, is capable of localizing an electron-hole pair (exciton). The wave functions and the binding energy of these localized excitons are obtained and their optical characteristics are calculated.

PACS numbers: 71.35. + z, 71.50. + t

Point defects in semiconducting crystals, such as isoelectronic impurities, closely-located donor-acceptor pairs, etc. produce short-range fields that influence the motion of the electrons and holes.[1] Despite the small effective radius r_0 of these fields (r_0 is equal to several lattice constants), their "power" can be sufficient to produce impurity levels in a forbidden band. If, however, no carrier localization takes place on the defects, then the short-range potential fields are centers of scattering of electrons and holes. Such scattering becomes resonant when the energies of the scattered particles are low,[2] i.e., the quasimomenta $k_{e,h}$ of the electrons and holes satisfy the condition $k_{e,h}r_0 \ll 1$. It can be said in this case that the defect produces a resonant (virtual) energy level in the corresponding band.[2] It is established in the present paper that resonant scattering can be the cause of exciton localization on defects that produce short-range fields. The resonant scattering of an electron contained in an exciton leads to a substantial increase of the electron density near the defects, and it is this which causes the effective attraction of the exciton hole to the defect. The hole, held near the defect by the produced effective protential, holds in turn the electron via the Coulomb field. Thus, the exciton becomes localized as a unit. The electrons and holes cannot be trapped separately by the defect and only carriers bound into an exciton pair can be localized. For such localized excitons, analytic expressions are obtained for the wave functions and for the binding energy, and the optical characteristics are calculated.

We consider a situation typical of isoelectronic impurities, when a point defect influences the motion of only one of the carrier, e.g., the electron. To describe the short-range field of the defect we shall use the zero-radius potential approximation[3,4]: the influence of the field reduces to specifying the boundary conditions for the wave function of the electron near the point defect. This approximation is justified, since the characteristic values of the electron quasimomentum in the exciton problem are $k_e \sim 1/a_B$ while $k_e r_0 \sim r_0/a_B \ll 1$ (a_B is the Bohr radius of the exciton). The equation for finding the wave function $\Psi(\mathbf{r}_e, \mathbf{r}_h)$ of the electron-hole pair in the presence of a zero-radius potential produced by the defect is of the form[3,4]

$$\left\{-\frac{\hbar^2}{2m_e}\Delta_e - \frac{\hbar^2}{2m_h}\Delta_h - \frac{e^2}{\varkappa|\mathbf{r}_e-\mathbf{r}_h|} - E\right\}\Psi(\mathbf{r}_e, \mathbf{r}_h) = -2\pi L\frac{\hbar^2}{m_e}\delta(\mathbf{r}_e)\frac{\partial}{\partial r_e}[r_e\Psi(\mathbf{r}_e, \mathbf{r}_h)]. \quad (1)$$

With the boundary condition

$$\frac{\partial}{\partial r_e}\ln[r_e\Psi(\mathbf{r}_e, \mathbf{r}_h)] = -\frac{1}{L} \quad \text{as} \quad r_e \to 0, \quad (2)$$

where $\mathbf{r}_{e,h}$ are the coordinates of the electron and the hole, measured from the impurity center, $\varkappa$ is the static dielectric constant, L is the scattering length of the electron by the defect, and $m_{e,h}$ are the effective masses of the corresponding carriers. If $L > 0$, bound states of the electron on the defect are possible, with a binding energy $-\hbar^2/2m_eL^2$. We, however, are interested in the case of negative scattering lengths $L < 0$, when the defect is incapable of trapping an electron. The perturbation it produces in the bottom of the conduction band leads to resonant scattering of free electrons, and the cross section of this scattering is[2]

$$\sigma = 4\pi L^2/(1+k_e^2L^2).$$

In a situation typical of semiconducting crystals, the effective mass of the hole noticeably exceeds the electrons mass: $m_h \gg m_e$. This makes it possible, when solving Eq. (1), to use the adiabatic approximation, according to which Ψ can be represented in the form

$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \chi(\mathbf{r}_h)\varphi(\mathbf{r}_e, \mathbf{r}_h), \quad (3)$$

where $\varphi(\mathbf{r}_e, \mathbf{r}_h)$ is the wave function of the electron in the Coulomb field of an immobile hole, $\chi(\mathbf{r}_h)$ is the wave function of an adiabatically slowly moving hole. The boundary conditions for the electron wave function are obtained by substituting (3) in (2):

$$\frac{\partial}{\partial r_e}\ln[r_e\varphi(\mathbf{r}_e, \mathbf{r}_h)] = -\frac{1}{L} \quad \text{as} \quad r_e \to 0. \quad (4)$$

We note that the wave function $\chi(\mathbf{r}_h)$ has no singularities as $\mathbf{r}_h \to 0$, since the hole does not interact directly with the defect. Leaving out of (1) terms that are small in $m_e/m_h \ll 1$, we have an equation for determining φ:

 0038-5646/83/020392-04$04.00

$$\left\{-\frac{\hbar^2}{2m_e}\Delta_e-\frac{e^2}{\varkappa|\mathbf{r}_e-\mathbf{r}_h|}-\varepsilon(\mathbf{r}_h)\right\}\varphi(\mathbf{r}_e,\mathbf{r}_h)$$
$$=-2\pi L\frac{\hbar^2}{m_e}\delta(\mathbf{r}_e)\frac{\partial}{\partial r_e}[r_e\varphi(\mathbf{r}_e,\mathbf{r}_h)], \quad (5)$$

where $\varepsilon(\mathbf{r}_h)$ is the energy of the electron in the Coulomb field of a hole in a zero-radius potential and depends parametrically on $\mathbf{r}_h$. The quantity $\varepsilon(\mathbf{r}_h)$ plays the role of a potential energy in the equation for the wave function of the hole:

$$\left\{-\frac{\hbar^2}{2m_h}\Delta_h+\varepsilon(\mathbf{r}_h)-E\right\}\chi(\mathbf{r}_h)=0. \quad (6)$$

Thus, to describe the motion of the exciton mass center, whose coordinates coincide with $\mathbf{r}_h$, it is necessary first of all to find $\varepsilon(\mathbf{r}_h)$.

If the electron-hole pair is infinitely far from the impurity center, the ground state of the pair is the ground state of exciton

$$\varepsilon(\mathbf{r}_h)\to E_0=-E_B=-\hbar^2/2m_e a_B^2 \quad \text{as} \quad r_h\to\infty.$$

The calculation of $\varepsilon(\mathbf{r}_h)$ reduces to finding the shift of the energy of the excitonic level in the presence of a zero-radius potential. The solution of (5) is the Coulomb Green's function

$$\varphi=\text{const}\, G(|\mathbf{r}_e-\mathbf{r}_h|, r_h, \varepsilon),$$

the explicit form of which was obtained in Ref. 5. Substitution of this solution in the boundary conditions (4) yields a transcendental equation for the energy spectrum of the system consisting of the exciton and the zero-radius potential, at arbitrary parameters L and r_h of the problem. The case considered by us, that of small scattering lenghts $|L|\ll a_B$, makes it possible to simplify substantially the procedure of finding the electron energy $\varepsilon(\mathbf{r}_h)$. Thus, the correction to the energy of the ground state of the exciton can be obtained by formally regarding the right-hand side of Eq. (5) as a perturbation that is small in $|L|/a_B\ll 1$ (Ref. 4):

$$\varepsilon(r_h)=E_0+U(r_h), \quad (7)$$

$$U(r_h)=2\pi L(\hbar^2/m_e)|\varphi_0(\mathbf{r}_h)|^2, \qquad \varphi_0(r)=e^{-r/a_B}(\pi a_B^3)^{-1/2}, \quad (8)$$

where $\varphi_0(r)$ is the wave function of the relative motion of the free exciton and $\mathbf{r}=\mathbf{r}_e-\mathbf{r}_h$. Substituting (7) in the mass-center equation of motion we obtain

$$\left\{-\frac{\hbar^2}{2m_h}\Delta_h+U(r_h)\right\}\chi(\mathbf{r}_h)=-I\chi(\mathbf{r}_h), \quad (9)$$

where $I=|E-E_0|$ is the absolute value of the binding energy of the exciton mass center. Thus, resonant scattering of an electron by a defect leads to the appearance of an effective potential $U(r_h)$ for the hole. The potential $U(r_h)$ (8) is known in the theory of atomic collisions as the potential of exchange interaction (electron exchange) between the atomic particles[1)] and can be both binding (attracting) and anti-binding (repelling).[4] In the case $L>0$, when the defect can produce a bound state with an isolated electron, the potential $U(r_h)>0$. An unusual situation is created: the defect that localizes the electron repels the exciton as a unit. This singularity in the behavior of U can be explained by recognizing that at $L>0$ the defect is capable of capturing an electron-hole pair. Such a capture, however, must be accompanied by destruction of the Mott exciton. The ground state of the system is in this case a state in which:

a) the electron ocupies a real "deep" level produced by the defect ($\hbar^2/2m_eL^2\gg E_B$), and its wave function is localized at distances $\sim L\ll a_B$ from the impurity center;

b) the electron attracts via the Coulomb interaction a hole whose wave function is also sufficiently strongly localized near the impurity center.

States of this type were investigated in Refs. 1 and 6. Thus, the motion of the exciton as a whole in the field of a defect at $L>0$ constitutes an excited states of the system, and the exchange interaction of the exciton with the defect is an antibinding (repelling). At $L<0$, when the defect produces in the conduction band a virtual level, $U(r_h)$ is an attraction potential.

Solving in standard manner Eq. (9) with an effective attraction potential $U(r_h)(L<0)$, we obtain the following equation for the energy spectrum of the exciton mass-center motion of:

$$J_\nu(\beta)=0; \quad \beta=2\left[\frac{m_h}{m_e}\frac{|L|}{a_B}\right]^{1/2}; \quad \nu=\left[\frac{m_h}{m_e}\frac{I}{E_B}\right]^{1/2}, \quad (10)$$

where J_ν is a Bessel function of order ν. The normalized have functions $\chi(\mathbf{r}_h)$ then take the form

$$\chi(\mathbf{r}_h)=NJ_\nu(\beta e^{-r_h/a_B})/r_h, \quad (11)$$

where N is a normalization factor, equal to

$$N=\left[\frac{\varkappa_0}{2\pi}\Big/\beta J_{\nu+1}(\beta)\frac{\partial J_\nu(\beta)}{\partial\nu}\right]^{1/2}, \qquad \varkappa_0=\left[\frac{2m_h}{\hbar^2}I\right]^{1/2}. \quad (12)$$

The solution of Eq. (10) for the binding energy of the mass center was obtained with the aid of the tables of the roots of the Bessel functions. The quantity I is determined by the value of the dimensionless parameter β, and Fig. 1 shows a plot of $I=I(\beta)$ (curve 1) for the ground state of the motion of the mass center. Using the property of the roots of the Bessel functions, we can conclude that localization of an exciton on a point defect is possible only at localization-parameter values $\beta\geqslant\beta_0=2.4$. At $\beta<\beta_0$ the "power" of the produced ef-

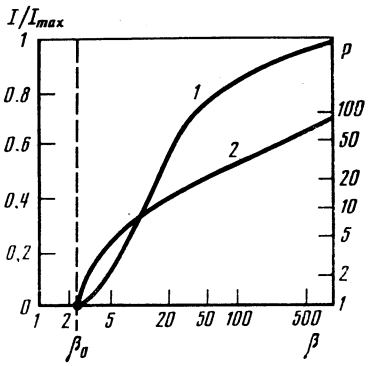

FIG. 1. Dependence of the binding energy of the mass center $I(\beta)/I_{\max}$ on the value of the localization parameter $\beta=2[(m_h/m_e)(|L|/a_B)]^{1/2}$ (curve 1) and the $P(\beta)$ dependence calculated from formula (21) (curve 2).

fective potential $U(r_0)$ is insufficient to hold the hole near the defect, and no localization takes place. The maximum mass-center binding energy I is reached at $\beta\to\infty$ ($m_h/m_e\to\infty$). In this case, according to Ref. 7, $\nu=\beta[1-O(\beta^{-2/3})]$ and

$$I=I_{max}\left[1-O\left(\frac{m_e}{m_h}\right)^{1/2}\right],$$
$$I_{max}=4(|L|/a_B)E_B. \tag{13}$$

The result (13) has a clear physical meaning: the binding energy I cannot exceed the maximum "depth" of the potential well $|U(r_h)|_{max}$, which is in fact equal to $4(|L|/a_B)E_B$ [Eq. (8)]. Thus, I_{max} determines the scale of the variation of the binding energy of the mass center of the exciton. In this case, in the entire interval of variation of the localization parameter β, the energy I is substantially less than the Bohr energy of the exciton:

$$I/E_B\leqslant 4|L|/a_B\ll 1.$$

It can be shown that as $\beta\to\infty$ the wave function of the hole for such a weakly bound exciton ($I\ll E_B$) is nevertheless localized in a smaller region near the defect, whose dimensions are $a\nu\sim a_B/\beta^{2/3}\ll a_B$.

Of particular interest is the behavior of the wave function $\chi(\mathbf{r}_h)$ and of the binding energy $I(\beta)$ near a critical value of the localization parameter $\beta\to\beta_0$. Using the asymptotic form of the Bessel functions as $\nu\to 0$ ($\beta\to\beta_0$), we have from (11)

$$\chi(\mathbf{r}_h)=\left(\frac{\varkappa_0}{2\pi}\right)^{1/2}\frac{e^{-\nu r_h/a_B}}{r_h}(1-e^{-2r_h/a_B}), \tag{14}$$

$$\nu=J_1^2(\beta_0)\beta_0(\beta-\beta_0)\approx 0.65(\beta-\beta_0), \tag{15}$$

$$I(\beta)=4\frac{|L|}{a_B}E_BJ_1^4(\beta_0)(\beta-\beta_0)^2\approx 0.073I_{max}(\beta-\beta_0)^2, \tag{16}$$

where $J_1(\beta_0)\approx 0.52$. The formula (16) obtained by us shows that near the critical values of the exciton-localization parameter of the binding energy of the exciton mass center to the defects depends quadratically on $(\beta-\beta_0)$, and this is a characteristic feature of the parametric behavior of weakly bound states.[2]

Let us calculate the optical characteristics of the considered localized exciton, namely, the probability W of their radiative recombination and the absorption coefficient $\alpha(\omega)$ of the radiation with formation of excitons that are bound on short-range defects. For direct-band semiconductors, calculations led to the following expression for W (Ref. 8):

$$W=\tau_{rad}^{-1}=B\left|\int\varphi(\mathbf{r}_h,\mathbf{r}_h)\chi(\mathbf{r}_h)d^3r_h\right|^2, \tag{17}$$

$$B=\frac{4e^2n\Omega}{3\hbar m_0^2c^3}|\langle c|\mathbf{p}|v\rangle|^2,\quad \Omega=\frac{1}{\hbar}[E_g-E_B-I], \tag{18}$$

where Ω is the frequency of the recombination photon, E_g is the width of the forbidden band, m_0 is the mass of the free electron, n is the refractive index, and $\langle c|\mathbf{p}|v\rangle$ is the optical matrix element of the interband transition. The relative-motion wave function $\varphi(\mathbf{r}_e,\mathbf{r}_h)$ agrees at $\mathbf{r}_e=\mathbf{r}_h$, apart from terms that are small in $|L|/a_B\ll 1$, with the wave function of the relative motion in the free exciton:

$$\varphi(\mathbf{r}_h,\mathbf{r}_n)=(\pi a_B^3)^{-1/2}[1+O(|L|/a_B)]. \tag{19}$$

Substituting (11) and (19) on (17), we obtain a final expression for W:

$$W=8B\nu^{-3}P(\beta), \tag{20}$$

$$P(\beta)=\frac{(\beta/2)^{2\nu}}{\beta J_{\nu+1}(\beta)\partial J_\nu(\beta)/\partial\nu}\left[\sum_{k=0}^{\infty}\frac{(-1)^k(\beta/2)^{2k}}{k!\Gamma(1+k+\nu)(1+2k/\nu)^2}\right]^2, \tag{21}$$

where $\nu=\nu(\beta)$ are the roots of Eq. (10). The dependence $P=P(\beta)$, calculated from Eq. (21), is shown in Fig. 1 (curve 2). For a binding energy I located in the region of the critical value of the localization parameter $\beta\to\beta_0$, when $\nu=[(m_h/m_e)(I/E_B)]^{1/2}\ll 1$, the formula for W assumes the simplest form: $P(\beta)\to 1$ as $\beta\to\beta_0$ and

$$W=8B\nu^{-3}\approx 30B(\beta-\beta_0)^{-3}. \tag{22}$$

This behavior of the radiative-recombination probability is typical of bound excitons whose mass-center wave-function dimensions greatly exceed the dimensions of the exciton itself ($a_\nu\sim a_B/\nu\gg a_B$): $W\propto\nu^{-3}\propto I^{-3/2}$ (Ref. 8). The absorption coefficient $\alpha(\omega)$ of the optical radiation with formation of excitons bound to a resonantly scattering defect is

$$\alpha(\omega)=\frac{64\pi^2e^2}{m_0^2nc\Omega}\nu^{-3}P(\beta)|\langle c|\mathbf{ep}|v\rangle|^2\delta(\hbar\omega-\hbar\Omega), \tag{23}$$

where $\mathbf{e}$ is the polarization vector of the absorbed light. In deriving (23), the width of the exciton absorption lines was assumed infinitely small.

The formulas obtained by us for the effective potential $U(r_h)$ are valid only when the shift of the exciton energy levels is small. Strictly speaking, as $r_h\to 0$, the use of the zero-radius potential for a short-range field of a defect results in the electron falling on the Coulomb center: $\varepsilon(r_h)\propto\ln r_h$. An analysis of the exact equation for finding the spectrum of the exciton + zero-radius potential system shows that the energy shift of the exciton levels becomes noticable ($\gtrsim E_B$) when $r_h\lesssim\Delta=a_B\exp(-a_B/|L|)$. It is clear that in the case $|L|\ll a_B$ considered by us the value of Δ does not exceed the lattice constant (e.g., $\Delta\sim 7\times 10^{-3}\,a_B$ already at $|L|=(1/5)a_B$). Therefore, the formulas obtained on the basis of the model of the zero-radius potential describe correctly the shift of the exciton energy levels in the entire real interval of variation of r_h. In a special investigation of the case $r_h=0$, when the hole for some reason is located directly on the defect, the potential of a point defect should be more readily represented in the form of a well of small but finite width, over the dimensions of which the Coulomb interaction between the electron and the hole becomes cut off. As shown by Zel'dovich,[9] the energy shift of the exciton levels is in this case also described by expression (8).

In conclusion, let us formulate the main features of the process of localization of excitons on defects that produce resonant levels.

1. A defect that produces resonant levels without binding the carriers separately is capable of localizing an electron-hole pair — an exciton. Processes of this kind were ex-

perimentally observed for isoelectronic impurities.[10] In Ref. 6, a variational method was used to calculate the binding energy of an exciton to an isoelectronic impurity, and the numerical results of the calculation confirmed the possibility of the localization considered above (we note that in Ref. 6 the choice of the variational parameters for the region close to the exciton localization threshold corresponded to large values of the scattering length, $|L| \gg a_B$.)

2. The possibility of localization and the binding energy of the mass center of the exciton are determined by the value of dimensionless parameter $\beta = 2[(m_h/m_e)(|L|/a_B)]^{1/2}$. Capture of the exciton by a defect is possible only at values $\beta \geqslant \beta_0 \approx 2.4$.

3. An exciton localized in such a defect is always weakly coupled to it: $I \ll E_B$. The characteristic dimension of the wave function of the mass center is determined by the quantity β: as $\beta \to \infty$ we have $a_\nu \sim a_B/\beta^{2/3}$, while for the critical values $\beta \to \beta_0$ we obtain $a_\nu \sim a_B/(\beta - \beta_0)$.

4. Excitons localized on resonant levels can make a noticeable contribution to the absorption and to optical luminescence of semiconducting crystals.

An isoelectronic defect capable of producing resonant levels can be a donor-acceptor pair with small distance between the impurity atoms (distance on the order of the lattice constant). Such resonant levels, by influencing on the motion of the electron-hole pair—of the intermediate exciton,[11]—can substantially increase the probability of the "inter-impurity" radiative recombination.

The case $|L| \ll a_B$ considered in this paper make it possible to obtain simple analytic expressions for the physical quantities of interest to us. When ascertaining the possibility of localization of excitons in the other limiting case $|L| \gg a_B$ (the resonant level practically coincides with the position of the conduction-band boundary), numerical calculations are necessary.

The author thanks I. P. Ipatova and V. I. Perel' for constant consultations and a discussion.

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Translated by J. G. Adashko