Exchange Interaction in Bound Excitons in Semiconductors

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The exchange interaction is considered in semiconductor excitons which are localized on defects such as isoelectronic traps and ionized donors (acceptors). It is shown that the exchange interaction of the bound excitons is distinguished by a number of features in comparison with that of free excitons. The magnitude of the exchange interaction depends in an essential way on the nature of the defect, and it may be either larger or smaller than the exchange interaction in a free exciton. In addition, in the case of a bound exciton the annihilation interaction also gives a contribution to the exchange, where in the case of free excitons this leads to a difference in the energies of longitudinal and transverse excitons.

The exchange splitting of the exciton lines in semiconductors, which was first observed as long ago as 1960,[1] has recently become an object of detailed investigation. In a number of articles[2] it was shown that taking account of the exchange interaction in many cases turns out to be very important in connection with the interpretation of exciton spectra and, in particular, their changes under deformation, and also in the presence of a magnetic field.

At the present time in many semiconductors, along with the free excitons bound excitons are also observed and studied, the latter being localized on neutral and charged centers, and moreover it has recently become possible to also observe the exchange splitting in such excitons.[3] In this connection, an investigation of the exchange interaction in bound excitons is of interest.

As the calculations presented below show, the exchange splitting of the bound excitons is distinguished by a number of features; in particular, its value depends on the nature of the center and may differ appreciably from the value of the exchange splitting of a free exciton.

1. The theory of the exchange interaction for free excitons has been developed in a number of articles.[4-7] In these articles it was shown that the exchange interaction of the free excitons is related to the short-range part of the potential describing the interaction between electron and hole.

According to Eqs. (36) and (37) of article [7], in the case of arbitrary degeneracy of the bands, the operator for the exchange interaction between electron and hole has the following form in the coordinate representation:

$$\mathscr{H}^{\text{ex}}_{m'n',mn}(\mathbf{r}'\mathbf{R}',\mathbf{r}\mathbf{R}) = \mathscr{V}\langle m'\mathscr{K}n|V|\mathscr{K}n'm\rangle\delta(\mathbf{r})\delta(\mathbf{r}')\delta(\mathbf{R}-\mathbf{R}'), \quad (1)$$
$$\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2,\quad \mathbf{R}=\mathbf{a}\mathbf{r}_1+\mathbf{b}\mathbf{r}_2,\quad \mathbf{a}+\mathbf{b}=\mathbf{I},$$

where

$$\langle m'\mathscr{K}n|V|\mathscr{K}n'm\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \psi^*_{m'\mathbf{k}_c}(\mathbf{x}_1)(\mathscr{K}\psi_{n\mathbf{k}_v}(x_2))^* V(\mathbf{r}_1-\mathbf{r}_2)\psi_{m\mathbf{k}_c}(\mathbf{x}_2)\mathscr{K}\psi_{n'\mathbf{k}_v}(\mathbf{x}_1). \quad (2)$$

Here $\mathbf{r}_{1,2}$ denote the coordinates of the electron and of the hole, $\mathscr{V}$ is the crystal volume, $V(\mathbf{r}_1-\mathbf{r}_2)$ is the potential of the interaction between electron and hole, $\psi_{m\mathbf{k}_c}$, $\mathscr{K}\psi_{n\mathbf{k}_v}$ denote the Bloch functions of a conduction electron and of the missing electron in the valence band, corresponding to a hole in the state $n\mathbf{k}_v$, $\mathscr{K}$ is the time reversal operator, and $\mathbf{k}_v$ and $\mathbf{k}_c$ denote the positions of the bands' extrema. The integration over $\mathbf{x}$ in Eq. (2) includes a summation over the spin indices. Since the Bloch functions are normalized to unity over the total volume, then the matrix element (2) is proportional to $\Omega_0/\mathscr{V}$, where Ω_0 denotes the volume of the elementary cell.

According to Eq. (26) of article [7], allowance for the exchange interaction between electrons in the valence band and in the conduction band in the $\mathbf{k}\cdot\mathbf{p}$-approximation, that is, allowance for only the long-range part of the interaction between electron and hole, leads to the potential

$$\mathscr{H}^a_{m'n',mn}(\mathbf{r}'\mathbf{R}',\mathbf{r}\mathbf{R}) = -\sum_{\alpha\beta} Q^{\alpha\beta}_{m'\mathscr{K}n,\mathscr{K}n'm}\frac{\partial^2 V(\mathbf{R}-\mathbf{R}')}{\partial R_\alpha \partial R_\beta}\delta(\mathbf{r})\delta(\mathbf{r}'), \quad (3)$$

$$Q^{\alpha\beta}_{m'\mathscr{K}n,\mathscr{K}n'm} = \frac{\hbar^2}{m^2E_g^2}p^\alpha_{m'\mathscr{K}n'}p^\beta_{\mathscr{K}nm},\quad V(\mathbf{R}) = -\frac{e^2}{\varkappa R}, \quad (4)$$

where $p^\alpha_{m'\mathscr{K}n'}$ denotes the matrix element of the momentum operator on Bloch functions at the bottom of the band, E_g denotes the width of the forbidden gap, and $\varkappa$ is the dielectric constant.

The operator (3) describes the annihilation interaction of the electron and hole, and for free excitons it does not lead to an exchange splitting, but to a splitting into longitudinal and transverse excitons. From the phenomenological theory[8] (see also formulas (53) and (54) of article [7]) it follows that in the annihilation interaction $\varkappa$ is the dielectric constant at the frequency of excitation of the exciton, after deducting the contribution to $\varkappa$ associated with the excitation of the exciton itself, that is, essentially the optical dielectric constant $\varkappa_\infty$.

Formulas (1)–(4) describe the electron-hole exchange interaction of both in free and in bound excitons in semiconductors. As will be shown below, for bound, direct excitons the annihilation interaction (3) also gives a contribution to the exchange splitting, in contrast to the case of free excitons. For bound excitons it is convenient to factor out the singular part $\nabla^2V(\mathbf{R}) = -4\pi e^2\varkappa^{-1}\delta(\mathbf{R})$ in formula (3), having rewritten (3) in the form

$$\mathscr{H}^a_{m'n',mn}(\mathbf{r}'\mathbf{R}',\mathbf{r}\mathbf{R}) = \sum_{\alpha\beta}\Big[\Big(Q^{\alpha\beta}_{m'\mathscr{K}n,\mathscr{K}n'm} - \frac{1}{3}\operatorname{Sp} Q_{m'\mathscr{K}n,\mathscr{K}n'm}\delta_{\alpha\beta}\Big) \times \frac{e^2}{\varkappa}\frac{1}{|\mathbf{R}-\mathbf{R}'|^3}\Big(\delta_{\alpha\beta} - \frac{3(R_\alpha-R_\alpha')(R_\beta-R_\beta')}{|\mathbf{R}-\mathbf{R}'|^2}\Big) + \frac{4\pi e^2}{3\varkappa}\operatorname{Sp} Q_{m'\mathscr{K}n,\mathscr{K}n'm}\delta(\mathbf{R}-\mathbf{R}')\Big]\delta(\mathbf{r})\delta(\mathbf{r}'),$$

where

$$\operatorname{Sp} Q_{m'\mathscr{K}n,\mathscr{K}n'm} = \sum_\alpha Q^{\alpha\alpha}_{m'\mathscr{K}n,\mathscr{K}n'm}.$$

2. In semiconductors an exciton can be localized either on charged or on neutral centers. Here one can distinguish the following types of bound excitons:

a) The exciton is localized on a charged donor or on an acceptor. The binding energy of such excitons has been calculated in a number of articles,[9,10] in which it was shown that such complexes cannot be formed for arbitrary ratios of the effective masses, since for close values of the masses the formation of a neutral donor (acceptor) with the release of a free hole (electron) is energetically more favorable. In this case the wave function $F(\mathbf{r}, \mathbf{R})$ of the bound exciton differs substantially from the wave function of the free exciton, and one can rather regard such a bound exciton as a neutral donor (acceptor), which has captured a hole (electron).

b) The exciton is localized on an isoelectronic trap. If the energy binding the electron (or hole) to the trap substantially exceeds the binding energy E_0 of the electron and hole, then the wave function $F(\mathbf{r}, \mathbf{R})$ of the bound exciton can be approximately written in the form of a product

$$F(\mathbf{r}, \mathbf{R}) = \varphi(\mathbf{r}_1) f(\mathbf{r}), \tag{6}$$

where $\mathbf{r}_1$ denotes the electron (hole) coordinates.

c) The exciton is localized on a shallow neutral donor (or acceptor). In this case, in contrast to cases (a) and (b), three particles enter into the complex, and therefore the exchange interaction between identical particles—that is, between the electrons (or holes)—plays a fundamental role. In the ground state, when the spins of the electrons (holes) are antiparallel, the exchange interaction is not present and the multiplicity of the degeneracy of the ground state is determined by the multiplicity of the degeneracy of the hole (electron) band at the extremum point.[1)]

Below we consider cases (a) and (b) in more detail, when only an electron and a hole enter into the complex, and therefore the exchange interaction between them is essential. In these cases for arbitrary degeneracy of the bands, the smooth wave function of the bound exciton, corresponding to the state j, is represented by the column of functions

$$F^j(\mathbf{r}, \mathbf{R}) = \begin{vmatrix} F^j_{m_1, n_1}(\mathbf{r}, \mathbf{R}) \\ F^j_{m_1, n_2}(\mathbf{r}, \mathbf{R}) \\ \cdots\cdots \\ F^j_{m_l, n_s}(\mathbf{r}, \mathbf{R}) \end{vmatrix}; \tag{7}$$

here l and s denote the multiplicities of degeneracy of the conduction band and valence band, and j takes values from unity to N, where N is the degeneracy of level j without taking the exchange interaction into account.

According to Eq. (1) the matrix $\mathscr{H}^{\mathrm{ex}}_{ij}$ has the form

$$\mathscr{H}^{\mathrm{ex}}_{ij} = \mathscr{V} \sum_{mnm'n'} V_{m'\mathscr{K}n,\, \mathscr{K}n'm} \int F^{*i}_{m'n'}(0, \mathbf{R}) F^j_{mn}(0, \mathbf{R})\, d\mathbf{R}, \tag{8}$$

and according to Eqs. (3) and (5) $\mathscr{H}^{\mathrm{a}}_{ij}$ is given by

$$\mathscr{H}^a_{ij} = \mathscr{H}^a_{1ij} + \mathscr{H}^a_{2ij},$$

where

$$\mathscr{H}^a_{1ij} = \frac{4\pi e^2}{3\varkappa} \sum_{mnm'n'} \mathrm{Sp}\, Q_{m'\mathscr{K}n,\, \mathscr{K}n'm} \int F^{*i}_{m'n'}(0, \mathbf{R}) F^j_{mn}(0, \mathbf{R})\, d\mathbf{R}, \tag{9}$$

$$\mathscr{H}^a_{2ij} = \frac{4\pi e^2}{3\varkappa} \sum_{\alpha\beta mnm'n'} \left(Q^{\alpha\beta}_{m'\mathscr{K}n,\, \mathscr{K}n'm} - \frac{1}{3} \mathrm{Sp}\, Q_{m'\mathscr{K}n,\, \mathscr{K}n'm} \delta_{\alpha\beta} \right)$$
$$\times \frac{3}{4\pi} \int \frac{1}{|\mathbf{R} - \mathbf{R}'|^3} \left(\delta_{\alpha\beta} - \frac{3(R_\alpha - R_\alpha')(R_\beta - R_\beta')}{|\mathbf{R} - \mathbf{R}'|^2} \right) F^{*i}_{m'n'}(0, \mathbf{R}) F^j_{mn}(0, \mathbf{R}') \times d\mathbf{R}\, d\mathbf{R}'. \tag{10}$$

Formulas (8)–(10) determine the matrices of the exchange interaction for bound excitons. It is seen that they are determined both by the matrices V and Q, which are evaluated with the aid of the Bloch functions at the bottom of the band, and by integrals of the smooth functions (7). In this connection the annihilation terms $\mathscr{H}^{\mathrm{a}}_1$ and $\mathscr{H}^{\mathrm{a}}_2$ also give contributions to the exchange splitting.

3. Let us consider the case when both bands are degenerate only with respect to the spin, and without taking the exchange interaction into account the equation for $F_{mn}(\mathbf{r}, \mathbf{R})$ reduces to four identical equations

$$(\mathscr{H}_0(\mathbf{r}, \mathbf{R}) - E) F(\mathbf{r}, \mathbf{R}) = 0.$$

The ground state corresponds to the orbitally nondegenerate solution $F_0(\mathbf{r}, \mathbf{R})$; in this connection the exciton's ground state is four-fold degenerate. One can label these degenerate states by the indices $j = \tilde{m}, \tilde{n}$ and

$$F^{\tilde{m}\tilde{n}}_{mn}(\mathbf{r}, \mathbf{R}) = F_0(\mathbf{r}, \mathbf{R})\, \delta_{\tilde{m}m} \delta_{\tilde{n}n}. \tag{11}$$

In this case according to (8) and (11) we have

$$\mathscr{H}^{\mathrm{ex}}_{m'n',\, mn} = \mathscr{V} V_{m'\mathscr{K}n,\, m\mathscr{K}n'} J, \quad J = \int |F_0(0, \mathbf{R})|^2 d\mathbf{R}, \tag{12}$$

whereas for a free exciton in this case, according to Eq. (38) of article [7] one has

$$\mathscr{H}^{\mathrm{ex}}_{m'n',\, mn} = \mathscr{V} V_{m'\mathscr{K}n,\, m\mathscr{K}n'} |f_0(0)|^2; \tag{13}$$

here the wave function of the free exciton is given by

$$F_0(\mathbf{r}, \mathbf{R}) = \mathscr{V}^{-1/2} f_0(r) e^{i\mathbf{K}\mathbf{R}}.$$

From (12) and (13) it follows that the matrix $\mathscr{H}^{\mathrm{ex}}$ has the same form for the cases of free and bound excitons, and the constant ratio is determined by the relation

$$\xi = \frac{1}{|f_0(0)|^2} \int |F_0(0, \mathbf{R})|^2 d\mathbf{R}. \tag{14}$$

For the function (11) the matrix operator $\mathscr{H}^{\mathrm{a}}_1$ has the form[2)]

$$\mathscr{H}^a_{1m'n',\, mn} = \frac{4\pi e^2}{3\varkappa} \mathrm{Sp}\, Q_{m'\mathscr{K}n,\, \mathscr{K}n'm} J. \tag{15}$$

In the case of simple bands the second term $\mathscr{H}^{\mathrm{a}}_2$ has the form

$$\mathscr{H}^a_{2m'n',\, mn} = \frac{4\pi e^2}{3\varkappa} \sum_{\alpha\beta} \left(Q^{\alpha\beta}_{m'\mathscr{K}n,\, \mathscr{K}n'm} - \frac{1}{3} \mathrm{Sp}\, Q_{m'\mathscr{K}n,\, \mathscr{K}n'm} \delta_{\alpha\beta} \right) I_{\alpha\beta},$$

[1)]If the exciton is localized on a deep neutral center—either a donor or an acceptor, then the exchange interaction between identical particles and particles of different signs may be of the same order of magnitude. The effective-mass approximation, which was used in the derivation of the cited formulas, is not applicable for such deep centers. In this case the Hamiltonian of the exchange interaction can be obtained by the method of invariants.

[2)]It is not difficult to show that, for all operations of the group $G_{\mathbf{k}_0}$ the matrix elements $V_{m'Kn,Kn'm}$ and Trace $Q_{m'Kn,Kn'm}$ transform in identical fashion; therefore the form of these matrices in identical bases coincides to within a constant. One should, however, keep in mind that as a consequence of the selection rule for the interband matrix elements of the momentum, the matrix Trace $Q_{m'Kn,Kn'm}$ vanishes in the case when direct transitions between the valence band and the conduction band are forbidden.

$$I_{\alpha\beta} = \frac{3}{4\pi}$$

$$\times \int \frac{1}{|\mathbf{R}-\mathbf{R}'|^3}\left(\delta_{\alpha\beta} - \frac{3(R_\alpha - R_\alpha')(R_\beta - R_\beta')}{|\mathbf{R}-\mathbf{R}'|^2}\right) F_0^*(0,\mathbf{R}) F_0(0,\mathbf{R}')\, d\mathbf{R}\, d\mathbf{R}'. \tag{16}$$

The integrals $I_{\alpha\beta}$ do not vanish only in the case when $F_0(0, \mathbf{R})$ has a symmetry lower than cubic.

One can express the contribution to the exchange splitting, associated with $\mathcal{H}^a$, in terms of the value ΔE of the energy splitting between longitudinal and transverse exciton. For this purpose, let us write $\mathcal{H}^a$ in the form

$$\mathcal{H}_{ij}^\alpha = \sum_\alpha A_i^\alpha A_j^{*\alpha} I + \sum_{\alpha\beta}\left(A_i A_j^{*\beta} - \frac{1}{3}\delta_{\alpha\beta}\sum_\gamma A_i^\gamma A_j^{*\gamma}\right) I_{\alpha\beta}, \tag{17}$$

where

$$A_i^\alpha = \left(\frac{4\pi e^2}{3\varkappa}\right)^{1/2} \frac{\hbar}{mE_g} p_i^\alpha, \tag{18}$$

i and j denote the collection of indices m′n′ and mn, and $p_i^\alpha = p^\alpha_{m'\mathcal{K}n'}$. The equations

$$\sum_s (\mathcal{H}_{is}^a - E\delta_{is})\Phi_s = 0$$

for the determination of the eigenfunctions Φ_i and the energy E of a matrix $\mathcal{H}^a$ of the type (17) have the form

$$E\Phi_i = J\sum_\alpha A_i^\alpha g_\alpha + \sum_{\alpha\beta}\left(A_i^\alpha g_\beta - \frac{\delta_{\alpha\beta}}{3}\sum_\gamma A_i^\gamma g_\gamma\right) I_{\alpha\beta}, \tag{19}$$

$$g_\alpha = \sum_i A_i^{*\alpha}\Phi_i. \tag{20}$$

For $E \neq 0$, having substituted Φ_i from Eq. (19) into (20), we obtain the following system of equations for the quantities g_α:

$$g_\alpha E = \sum_\beta g_\beta \Gamma^{\beta\alpha}, \tag{21}$$

where

$$\Gamma^{\beta\alpha} = J\sum_i A_i^\beta A_i^{*\alpha} + \sum_\gamma\left(\sum_i A_i^\gamma A_i^{*\alpha}\right) I_{\gamma\beta} \tag{22}$$

(here it is taken into account that $\mathrm{Tr}\, I = \sum_\gamma I_{\gamma\gamma} = 0$).

The displacement of the levels E, associated with $\mathcal{H}^a$, is determined by the equation

$$\mathrm{Det}|E\delta_{\alpha\beta} - \Gamma^{\beta\alpha}| = 0. \tag{23}$$

Since Eq. (23) is a cubic equation, then no more than three levels are split off in the general case due to the matrix $\mathcal{H}^a$. The energy of the remaining levels is not changed. It is not difficult to show that the quantity $\Gamma^{\alpha\beta}$ appearing in Eq. (23) transforms like the components of the tensor $x_\alpha x_\beta'$ under the operations of the group $G_{\mathbf{k}_0}$. Since, on the other hand, this quantity must be invariant under all transformations of the group $G_{\mathbf{k}_0}$, then the number of nonvanishing, linearly independent quantities $\Gamma^{\alpha\beta}$ and, therefore, the form of Eq. (23) are determined by the number of invariants $x_\alpha x_\beta'$ in the group $G_{\mathbf{k}_0}$. Thus, in the case of cubic symmetry

$$\Gamma^{\alpha\beta} = \Delta\delta_{\alpha\beta}, \tag{24}$$

where

$$\Delta = \frac{4\pi e^2}{3\varkappa}\frac{\hbar^2}{m^2E_g^2}\sum_{mn}|p^z_{m\mathcal{K}n}|^2 J;$$

in this connection $I_{\alpha\beta} = 0$.

Thus, from Eqs. (23) and (24) it follows that for cubic symmetry $G_{\mathbf{k}_0}$ the matrix $\mathcal{H}^a$ leads to a splitting of the three levels having the same energy (these three levels correspond to states with total spin S = 1), and the remaining level (the level with S = 0) remains unshifted.

According to Eq. (54) of [7], in the case of a simple band the shift of the ground state terms of a free exciton as a consequence of the annihilation interaction is determined by the expression (neglecting the exchange splitting given by Eq. (13))

$$\Delta E(\mathbf{K}) = \frac{4\pi e^2}{\varkappa}\frac{\hbar^2}{m^2E_g^2}|f_0(0)|^2\sum_{mn} p^\alpha_{m\mathcal{K}n}p^\beta_{\mathcal{K}nm}\frac{K_\alpha K_\beta}{K^2}. \tag{25}$$

Therefore, for the case of cubic symmetry the difference between the energies of longitudinal and transverse excitons is given by

$$\Delta E = \frac{4\pi e^2}{\varkappa}\frac{\hbar^2}{m^2E_g^2}|f_0(0)|^2\sum_{mn}|p^z_{m\mathcal{K}n}|^2. \tag{26}$$

Thus, in this case the ratio of the magnitude of the exchange splitting of a bound exciton, due to the annihilation interaction, to the value of the longitudinal exciton's splitting is given by

$$\frac{\Delta}{\Delta E} = \frac{1}{3}\frac{J}{|f_0(0)|^2} = \frac{\xi}{3}. \tag{27}$$

For a nondegenerate band and for cubic symmetry, the exchange interaction Hamiltonian has the form

$$\mathcal{H}^{\mathrm{ex}} = \Delta_0 + \Delta_1(\sigma\sigma'), \tag{28}$$

where σ and σ' are the Pauli matrices in the basis of the electron and hole functions. According to Eqs. (12) and (27)

$$\Delta_0 = \xi\left(\Delta_0^0 + \frac{\Delta E}{4}\right), \quad \Delta_1 = \xi\left(\Delta_1^0 + \frac{\Delta E}{12}\right), \tag{29}$$

where Δ_0^0 and Δ_1^0 denote the corresponding constants for a free exciton.

For uniaxial crystals the tensor Γ has two distinct components: $\Gamma_{xx} = \Gamma_{yy} = \Gamma_\perp$, $\Gamma_{zz} = \Gamma_\parallel$. Therefore, according to Eq. (23) in the general case one of the levels is shifted by the amount

$$\Delta_\parallel = \Gamma_\parallel = \frac{4\pi e^2\hbar^2}{3\varkappa m^2E_g^2}\sum_{mn}|p^z_{m\mathcal{K}n}|^2(J + I_{zz}), \tag{30}$$

as a consequence of the annihilation interaction, and two of the levels are shifted by the amount

$$\Delta_\perp = \Gamma_\perp = \frac{4\pi e^2\hbar^2}{3\varkappa m^2E_g^2}\sum_{mn}|p^x_{m\mathcal{K}n}|^2\left(J - \frac{I_{zz}}{2}\right). \tag{31}$$

In contrast to the case of a cubic crystal, in a uniaxial crystal the longitudinal-transverse splitting of a free exciton depends on the direction of the vector **K**: $\Delta E(K_x) = \Delta E(K_y) = \Delta E_\perp$ is not equal to $\Delta E(K_z) = \Delta E_\parallel$. One can easily obtain explicit expressions for $\Delta E_\perp$ and $\Delta E_\parallel$ from Eq. (25). By comparing them with expressions (30) and (31), we find that the ratio of the annihilation splitting of a bound exciton and the longitudinal-transverse splitting of a free exciton is given by

$$\Delta_\parallel / \Delta E_\parallel = {}^1/_3(\xi + \xi'), \quad \Delta_\perp / \Delta E_\perp = {}^1/_3(\xi - \xi'/2), \tag{32}$$

where $\xi' = I_{zz}/|f_0(0)|^2$.

For example, for the group C_{6v} and for the excitons $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ the exchange Hamiltonian has the following form for the ground state:

$$\mathcal{H}^{ex} = \Delta_0 + \Delta_1(\sigma_z\sigma_z') + \Delta_2(\sigma_x\sigma_x' + \sigma_y\sigma_y') \quad (\Gamma_7 \times \Gamma_7),$$
$$\mathcal{H}^{ex} = \Delta_0 + \Delta_1(\sigma_z\sigma_z') \quad (\Gamma_7 \times \Gamma_9). \tag{33}$$

According to (32) the constants in (33) are given by

$$\Delta_0 = \xi[\Delta_0^0 + {}^1/_{12}(\Delta E_\parallel + 2\Delta E_\perp)] + {}^1/_{12}\xi'(\Delta E_\parallel - \Delta E_\perp),$$
$$\Delta_1 = \xi[\Delta_1^0 + {}^1/_{12}(2\Delta E_\perp - \Delta E_\parallel)] - {}^1/_{12}\xi'(\Delta E_\parallel + \Delta E_\perp),$$
$$\Delta_2 = \xi[\Delta_2^0 + {}^1/_{12}\Delta E_\parallel] + {}^1/_6\xi'\Delta E_\parallel,$$
$$(\Gamma_7 \times \Gamma_7). \tag{34a}$$

and

$$\Delta_0 = -\Delta_1 = \xi(\Delta_0^0 + {}^1/_6\Delta E_\perp) - {}^1/_{12}\xi'\Delta E_\perp, \quad (\Gamma_7 \times \Gamma_9). \tag{34b}$$

4. Now let us estimate the quantity ξ for the two exciton models indicated above, localized on charged and isoelectron centers.

For case (b), that of an exciton localized on an isoelectronic trap and having a wave function approximately described by the function (6), we have $F(0, \mathbf{R}) = \varphi(\mathbf{R})f(0)$ and, consequently, with the normalization condition $\int|\varphi(\mathbf{R})|^2 d\mathbf{R} = 1$ taken into consideration we obtain

$$\xi = |f(0)|^2 \,/\, |f_0(0)|^2. \tag{35}$$

If the energy binding the electron (hole) to the trap is large, then $\varphi(\mathbf{r}_1)$ is a hydrogen-like function whose radius is determined by the effective mass m_h of the hole (m_e of the electron), whereas the radius of a free exciton is determined by the reduced mass $1/\bar{m} = 1/m_e + 1/m_h$. Therefore, in this approximation

$$\xi = \left(\frac{a_B^0}{a_B}\right)^3 = \left(\frac{m_h}{\bar{m}}\right)^3 = (1+\mu)^3, \quad \mu = \frac{m_h}{m_e}. \tag{36}$$

On the other hand, if the trap captures a hole, then $\xi = (1 + \mu^{-1})^3$. It is seen that in the case of the capture of an exciton by an isoelectronic trap, the exchange splitting of the bound exciton may substantially exceed the exchange splitting of the free exciton due to both the increase in f(0) as well as due to the contribution from the annihilation interaction, which is determined by the second term in (3).

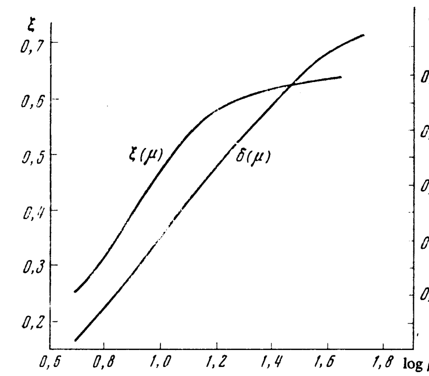
For case (a), where the exciton is localized on a charged center, as indicated above, the wave function is significantly different from the wave function of a free exciton and resembles the wave function of a molecular ion of hydrogen. Calculations of the energy binding the exciton to the charged center have been carried out in a number of articles by using a variational method.

In order to estimate the quantity ξ we shall use the variational function given in [10], since not only the energy values of the bound exciton are indicated in this article, but also the parameters of the wave function for different values of μ.

In [10] the wave function of the bound exciton was chosen in the form

$$F(\mathbf{r}_1, \mathbf{r}_2) = A[\exp\{-\alpha(r_1 + \Gamma r_2)\} + b\exp\{-\alpha(R + \Gamma' r_2)\}]r_2^h, \tag{37}$$

where $\mathbf{r}_{1,2}$ denote the electron and hole coordinates, respectively. The dependence of ξ on μ, obtained on the basis of the data of [10], is shown in the figure. There the difference between the energy binding the exciton to the complex and the binding energy E_d to a donor is shown in units of the energy E_d, that is, the quantity



The dependence of ξ and δ on $\mu = m_h/m_e$. $\xi(\mu)$ and $\delta(\mu)$ are plotted along the left-hand and the right-hand ordinates axes, respectively.

$$\delta(\mu) = [E(\mu) - E_d] \,/\, E_d = 2E'(\mu) - 1,$$

where $E'(\mu)$ denotes the energy $E(\mu)$ of a bound exciton in units of $m_e e^4/\hbar^2\kappa^2$. This quantity characterizes the stability of the bound exciton state. From the figure it is seen that the value of ξ increases as μ increases simultaneously with the value of δ, since with an increase of μ the hole approaches the center and the overlap of the electron and hole wave functions is increased. For large values of μ, the quantity $\xi \approx 0.65$, that is, the exchange splitting of the bound exciton becomes comparable with the exchange splitting of a free exciton. Near the limiting value $\mu \approx 5$, below which a bound exciton does not occur, $\xi \approx 0.25$.

In conclusion we note that in the case when several equivalent extrema exist in the valence band or in the conduction band, then orbital-valley splitting, which is well-known for shallow impurity centers in semiconductors, can be observed in bound excitons (direct or indirect); this splitting connects the states near different extrema. For free excitons, just as for free carriers, such splitting is not present. In this case the nature of the exchange splitting for bound excitons depends on the ratio of the exchange splitting Δ_{ex} to the orbital-valley splitting Δ_c.

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44