PHYSICAL REVIEW B **75**, 245410 (2007)

Intermediately bound exciton in a quantum well doped with transition metal impurities

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(Received 18 October 2006; revised manuscript received 1 April 2007; published 8 June 2007)

The possibility of an intermediately bound exciton in a quantum well, doped with transition metal impurities, is considered. Such bound excitons, in which both carriers are captured in an intermediate-radius orbital, can appear in a quantum well due to strong hybridization of the two-dimensional band states and the impurity *d* states that are strongly suppressed in the bulk case due to symmetry considerations. The difference between the bound exciton in T_d (zinc-blende) bulk semiconductors and in the quantum well is due to the lower symmetry of the latter, namely, a tetragonal D_{2d} symmetry. In bulk systems, the outer carrier is bound by the Coulomb field of the first exciton carrier and may be considered to be within the framework of the hydrogen-like model. On the other hand in the quantum well, the central-cell pseudopotential appears to be the leading attracting potential for the outer carrier and can be described using Koster and Slater's model. These differences in binding mechanisms may lead to striking differences in the structure of the exciton spectra and in other magneto-optical properties.

DOI: 10.1103/PhysRevB.75.245410 PACS number(s): 73.21.Fg, 71.35.−y, 71.55.−i

I. INTRODUCTION

Excitons are typical excitations of electronic subsystems in semiconductors and molecular crystals. Two types of excitons are usually distinguished, namely, Frenkel and Wannier-Mott excitons. Frenkel excitons are strongly localized with a localization radius of the order of the atomic distance and are observed mainly in molecular crystals. Wannier-Mott excitons, on the other hand, are found mainly in semiconductors, their localization radius essentially exceeds the lattice spacing and their wave functions can be described within the framework of the effective-mass theory. Defects and impurities can bind free Wannier-Mott excitons.

The possibility of the localization of Wannier-Mott excitons on charged impurities was first predicted by Lambert,[1] and was later studied in detail.[2–5] Excitons can also be localized on isoelectronic centers. Isoelectronic centers are neutral with respect to the lattice, but create a local potential well and are, therefore, capable of capturing an electron or a hole, depending on the chemical properties of the impurity. The excess carrier captured by the short-range potential attracts a carrier of the opposite sign. Hence, an electron-hole pair is localized on a center with hydrogenlike properties of donor or acceptor type. The exciton localization mechanism was proposed by Hopfield *et al.*[6] and was confirmed by Cohen and Sturge.[7] Since then, this complex excitation in semiconductors has been studied both experimentally and theoretically.[8–14]

It is known that, as a rule, 3*d* transition elements in A_xB_{8-x} compounds form isoelectronic impurity centers with a d^n configuration of the incomplete shell.[15] Like other isoelectronic impurities, these impurities are also known to bind excitons. Unlike simple neutral impurities, however, isoelectronic transition metal (TM) impurities capture one carrier in their electrically active *d* shell, i.e., in the deep level of this impurity, and the second carrier is attracted by the Coulomb potential of the first carrier. In the excitation spectra, such bound excitons are observed as lines in the low-energy onset of the charge-transfer band. Involvement of the impurity *d* shell in the formation of the bound exciton is manifested by various features, e.g., possible multicharge states of the TM impurities and the amphoteric behavior of the excitons.[16] These deeply bound excitons (DBEs) have been studied extensively, both experimentally[17–21] and theoretically.[16,22] See Ref. 23 for a general review of the subject.

Isoelectronic 3*d* elements in bulk semiconductors can also form an intermediately bound exciton (IBE), which was observed and explained for Ni in CdS (Ref. 24) and Cu in ZnO.[25] This kind of exciton, in which both carriers are captured in intermediate-radius orbitals, results from the lower, wurtzite type of the crystalline environment of both CdS:Ni and ZnO:Cu systems compared with that of the zinc-blende symmetry in other systems. Such IBEs were found to be responsible for a significant change in the complex excitation spectra and in other properties. The idea that these excitations are due to intermediately bound excitons is supported also by additional experimental data on their isotope shifts and relaxation behavior.[26]

The effect of impurities on various kinds of exciton states (e.g., charged or neutral bound excitons) in a quantum well (QW) has received much attention over the years. Donor-related complexes in QW were proposed by Shanabrook and Comas.[27] Excitons bound to ionized donors located at the center of the QW,[28–30] as well as to isoelectronic impurities,[28,29,31–33] have also been studied both theoretically and experimentally.

In this paper, we present a microscopic theory of excitons bound to isoelectronic transition metal impurities in QW. The different properties of bound excitons in simple and structured isoelectronic impurities are presented. Such differences are connected to the properties of the *d* level and to the crystalline symmetry: three-dimensional (3D) systems crystallize in a tetrahedral lattice (T_d group), whereas the T_d symmetry in QW is lowered to a tetragonal D_{2d} symmetry. We show that while 3D systems with a T_d symmetry (e.g., GaAs and ZnS) form a DBE with a hydrogenlike spectrum, the quantum well made by the same material forms an intermediately bound exciton with a Koster-Slater-type single state. The lower symmetry of the crystalline environment of the substitutional impurity results in the essential modification of the wave functions of electrons localized around the impurity. This eventually leads both to a transformation of the deeply bound excitons into intermediately bound excitons and to partial equalizing of the behavior of the electron and hole that constitute the bound exciton. This equalization means that, unlike the standard cases in which excitons are bound to neutral impurities, both bound carriers acquire features of localized, deeply bound d states. It is shown that, in addition to the attraction of the first carrier by the short-range impurity potential, the outer carrier is attracted by the short-range pseudopotential, whereas the Coulomb potential leads only to small corrections. As an example, we consider bound excitons in III-V compounds.

II. GENERAL MODEL

Excitons that are bound to $3d$ impurities in QW are similar in many aspects to those deeply bound to common neutral impurities in the bulk case. Both are characterized by multielectron impurity configurations $[A^{(-)}(d^{n-1}+e),h]$ and $[A^{(+)}(d^{n-1}+h),e]$ for acceptor- and donor-type excitons, respectively. Here $A^{(\pm)}$ represents the impurity configuration whose shell either possesses or lacks an extra electron. As an example, we choose an acceptor-type bound exciton with a binding energy defined as the energy required to capture a free electron-hole pair[23]

$$E_{bex}=E(d^n,h)-E(d^{n-1}). \tag{1}$$

This expression produces an energy that is close to that of deep levels, i.e., the exciton line appears in the optical spectra as satellites at the edges of the impurity charge-transfer bands. The multielectron function Eq. (1) is constructed using the eigenfunction of the single-electron Hamiltonian of the impurity located in the QW

$$H_e=H_0+V_d(\mathbf{r}-\mathbf{R}_0)+U'(\mathbf{r}-\mathbf{R}_0), \tag{2}$$

where H_0 is the Hamiltonian describing the motion of an electron in the conduction and valence bands with an effective mass m^*, which is confined in the z direction by the potential $V(z)$. $U'(\mathbf{r}-\mathbf{R}_0)$ is the lattice crystal-field potential acting on the impurity at site $\mathbf{R}_0$, and $V_d(\mathbf{r})$ is the d-impurity potential. The effect of the periodic lattice potential is taken into account in the effective-mass approximation, which may be used since we are interested in the properties of states near the bottom of the lowest conduction band. The band wave functions then assume the form of

$$\varphi_{\lambda,j}(\mathbf{r})=\psi_{a\mathbf{k}_\parallel}(\rho)\chi_j(z). \tag{3}$$

Here λ and j are the quantum numbers describing the finite electron motion, ρ, in the xy plane and in the z direction, respectively, where $\lambda\equiv a\mathbf{k}_\parallel$ and a represents an electron or a hole in the conduction and valence bands, respectively. $\chi_j(z)$ are eigenfunctions of the confining potential $V(z)$. The hole wave function $\psi_{i\gamma}^{(h)}$ is an eigenfunction of the Hamiltonian $-H_v(\mathbf{r})$ of the valence band, with one electron removed. After excluding the core part of the impurity pseudoion, d^{n-1}, the general Schrödinger equation is reduced to the following two-particle equation

$$[H_e(\mathbf{r}_1)+H_h(\mathbf{r}_2)+U(\mathbf{r}_1-\mathbf{r}_2)-E_I^{ex}]\times\hat{A}\,\psi_{i\Gamma}^{(n)}(\mathbf{r}_1)\psi_{i\gamma}^{(h)}(\mathbf{r}_2)=0, \tag{4}$$

where the exciton energy, E_I^{ex}, is simply the difference between the total energies of the system with and without the exciton, $\psi_{i\Gamma}^{(n)}$ is the wave function of the nth electron, and $U(\mathbf{r}_1-\mathbf{r}_2)$ is the electron-hole Coulomb interaction. Here the indices Γ and γ correspond to the electron and hole quantum numbers in the irreducible representation, respectively.

Since the electron wave function is more localized than the hole wave function, the single-electron Schrödinger equation

$$[H_e+E_{i\Lambda'}(d^{n-1})-E]\psi_{i\Gamma}^{(n)}(\mathbf{r})=0 \tag{5}$$

is considered first, and the electron-hole Coulomb interaction, $U(\mathbf{r}_1-\mathbf{r}_2)$, is neglected. This equation determines the position of the $E_{i\Gamma}^{(n)}$ level of the (n)th bound electron and its wave function $\psi_{i\Gamma}^{(n)}(\mathbf{r})$ in the potential $U_{d\Gamma}(\mathbf{r})$ created by the $d^{(n-1)}$ core of the impurity d shell with the energy $E_{i\Lambda'}(d^{n-1})$.

Similarly, the following equation:

$$\left[\left(\hat{T}+\sum_j U_h'(\mathbf{r}-\mathbf{R}_j)+V(z)+U_{d\gamma}(\mathbf{r})\right)+U(\mathbf{r})-E_h\right]\psi_{i\gamma}^{(h)}(\mathbf{r})=0, \tag{6}$$

can be derived from Eq. (4) for the hole wave function, where $E_h=E-E_{i\Gamma}^{(n)}$. The Coulomb potential $U(\mathbf{r})$ arises due to the interaction between the hole and the nth electron in the d shell of the impurity ion, and $U_h'(\mathbf{r}-\mathbf{R}_j)$ is the periodic potential of lattice with the lack of the impurity site.

In the case of conventional isoelectronic d impurity in T_d bulk semiconductors, Eqs. (5) and (6) lead to a standard bound exciton (see, for instance, Refs. 6, 20, and 34). Many features were analyzed in Refs. 16 and 22, but the possibility of forming an electron-hole pair with comparable radii in QW requires special consideration. This mechanism, therefore, should be revised as in the case of a wurtzite-type lattice (C_{6v} hexagonal group).[24,25] Special attention should be paid to the short-range central-cell pseudopotential, which will be shown to play an important part in the formation of bound excitons in QW. In the two following sections, we will consider the difference between degrees of localization of both electron and hole pair. In order to investigate the electron-hole carriers, as described by Eqs. (5) and (6), we will consider the example of the electronic properties of a TM impurity in a GaAs quantum well.

III. TIGHTLY BOUND ELECTRON

We first describe, using the resonance scattering model, how an electron interacts with a single isoelectronic TM impurity centered in a QW. From the general theory of $3d$ impurities in semiconductors,[35–38] we know that the shape of the wave function and the position of the impurity deep level are determined largely by the covalent hybridization of the impurity d orbitals with the band states of the host material. To solve Eq. (5), we use the set of functions $\{\tilde{\varphi}_{\lambda,j},\psi_{d\Gamma\mu}\}$ as our basis for the expansion of the localized electron wave function. This set includes (i) the atomic d orbital, $\psi_{d\Gamma\mu}$, that forms the "core" of the impurity wave function, which retains its 3D character because its radius, r_d, is small in comparison with the width of the well, $V(z)$, which is responsible for the confinement in the z direction wave functions; and (ii) the wave functions of the quantum-well states, which should be orthogonalized to the d-electron wave functions

$$\tilde{\varphi}_{\lambda,j} = \varphi_{\lambda,j} - \sum_{\Gamma\mu} \langle d\Gamma\mu|\lambda,j\rangle \psi_{d\Gamma\mu}.$$

The energy level of the electron in the $d^{(n)}$ shell, $E_{i\Gamma}^{(n)}$, is then determined by the equation

$$E_{i\Gamma} = \varepsilon_{\Gamma}^{(n)} + \Delta U + M(E_{i\Gamma}), \tag{7}$$

where the potential part of the impurity scattering is negligible compared with the resonant scattering by the d level of the unfilled impurity shell. Here, the n electron ionization energy is defined as

$$\varepsilon_{\Gamma}^{(n)} = E(d^n) - E(d^{n-1}),$$

ΔU is the renormalization energy due to the response of the host states to the excess impurity charge,[35]

$$M(E_{i\Gamma}) = \sum_{\lambda j} \frac{|V_{\Gamma\mu,\lambda j}|^2}{E_{i\Gamma} - E_{\lambda j}} \tag{8}$$

is the self-energy part, and

$$V_{\Gamma\mu,\lambda j} = \langle d\Gamma\mu|U'(\mathbf{r}-\mathbf{R}_0)|\widetilde{\lambda j}\rangle \tag{9}$$

is the hybridization matrix element responsible for the mixing of atomic and band states in the above basis.

The wave function of the nth electron consists of a localized core and an extended Bloch tail,

$$\psi_{i\Gamma\mu}^{(n)} = [1/\sqrt{1+\tilde{M}'_{a\Gamma}}][\psi_{d\Gamma} \pm \sqrt{\tilde{M}'_{a\Gamma}}\psi_{b\Gamma}], \tag{10}$$

where

$$\tilde{M}'_{a\Gamma} = -d\tilde{M}_a(E_{i\Gamma})/dE_{i\Gamma}$$

and

$$\sqrt{\tilde{M}'_{a\Gamma}}\psi_{b\Gamma} = \sum_{j,\lambda} \frac{V_{\Gamma\mu,\lambda j}}{E_{i\Gamma} - E_{j,\lambda}} \tilde{\varphi}_{j,\lambda}.$$

It is known that in bulk semiconductors, the states in the lower part of the conduction band have only a weak influence on the electronic structure of 3d impurities in zinc-blende crystals since these states are formed predominantly by the s orbitals, which can form only nonbonding states with TM d orbitals.[15,39] As a result, the hybridization matrix elements of Eq. (9) are propotional to the absolute value k of the wave vector near the bottom of the conduction band. The main contribution to the tail part is, therefore, the antibonding combination from the heavy-hole band [denoted by the minus sign in Eq. (10)]. Since the impurity level position is counted from the top of the valence band, the level in the upper part of the forbidden energy gap appears to be very deep. This means that the Bloch tail, $\psi_{b\Gamma}$, of the wave function Eq. (10), is rather short ranged and has relatively little weight in the impurity wave function compared with that of the atomic d function, $\psi_{d\Gamma}$. This weight is proportional to the factor $\tilde{M}'_{a\Gamma}$ (shown in Fig. 1 of Ref. 24).

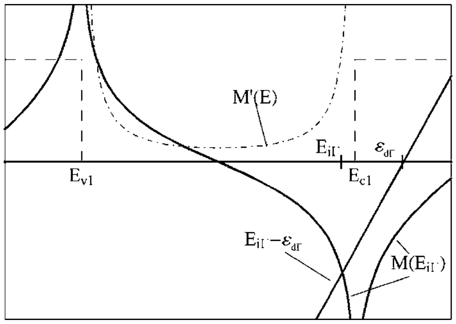

FIG. 1. Qualitative graphical solution of Eq. (7) for the first exciton carrier (electron) in a quantum well. The sum of the Hilbert transform is shown (solid line) with the singularities near the band edges (dashed line), which are typical for constant density of states. The intersection of this curve with the straight line $E_{i\Gamma}-\varepsilon_{d\Gamma}$ is the eigenvalue, $E_{i\Gamma}$. The shape of the function $\tilde{M}'_{c\Gamma_6}$ is also shown (dot-dashed line).

In a QW, the situation with respect to the same level is quite different: The presence in the integral of the envelope function, $\chi_j(z)$, lifts the selection rules for the hybridization integrals since this axially symmetric function contains all spherical harmonics, Y_{l0}. It is instructive to review the symmetries of the states, as follows:[40] The conduction-band s states and the valence-band p state are represented in the cubic zinc-blende T_d group as ${}^1\Gamma_1$ and ${}^3\Gamma_5$, respectively. In the double group representation, which takes into account electron spin, the ${}^1\Gamma_1$ conduction band becomes ${}^2\Gamma_6$ and ${}^3\Gamma_5$ transforms into ${}^2\Gamma_7+{}^4\Gamma_8$. Spin-orbit coupling splits off the ${}^2\Gamma_7$ and ${}^4\Gamma_8$ bands, leaving the ${}^4\Gamma_8$ as the ground state of the holes. In a quantum well, which lowers the T_d symmetry to D_{2d}, this band is split into ${}^2\Gamma_6$ (light-hole) and ${}^2\Gamma_7$ (heavy-hole) bands.

The resulting bound d electron states with crystal-field splitting transform according to irreducible representations Γ_3 and Γ_5. However, accounting for the spin-orbit interaction in the T_d group (see, e.g., Ref. 15), the Γ_3 becomes Γ_8 and Γ_5 states split into $\Gamma_8+\Gamma_7$ states. After lowering symmetry, the newly split representations ${}^2\Gamma_6+{}^2\Gamma_7$ of the tetragonal D_{2d} replace the ${}^4\Gamma_8$ of T_d. As a result, the wave function of the nth electron in the d shell of the charged $A^{(-)}$ ion, which transforms according to representation ${}^2\Gamma_6$, hybridizes strongly with both valence- and conduction-band states so that both matrix elements $V_{\Gamma_6,c}$ and $V_{\Gamma_6,v}$ [see Eq. (9)], are constant at $k_\parallel \to 0$.

The nonzero hybridization of the d levels with the states near the bottom of the conduction band can radically change the structure of the impurity states in quantum wells in comparison with those in the bulk case. The basic equation of the theory responsible for this difference is the self-energy part, $M(E)$, which is the principle part integral of Eq. (8)

$$M(E_{i\Gamma_6}) = \sum_{aj} \int \frac{S_{\Gamma_6 aj}(\varepsilon) d\varepsilon}{E_{i\Gamma_6} - E_j - \varepsilon}. \tag{11}$$

This integral is a conventional Hilbert transform of the local partial densities of states, $S_{\Gamma_6 aj}(\varepsilon) = \Sigma_{\mathbf{k}_\parallel} |V_{\Gamma_6,aj}(\mathbf{k}_\parallel)|^2 \delta(\varepsilon - \varepsilon_{aj\mathbf{k}_\parallel})$. The mass operator $M(E)$ estimated under the assumption of a constant hybridization parameter becomes

$$M(E_{i\Gamma_6}) = \sum_{j=1} |V_{\Gamma_6,aj}|^2 (S_j - S_{j-1}) \ln \left| \frac{E_{i\Gamma_6 j} + D_j}{E_{i\Gamma_6 j} - D_j} \right|, \tag{12}$$

where $2D_j$ is the subband width and $S_j = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right) j$ is the two-dimensional constant density of states. The nonzero value of $V_{\Gamma_6,c}(k_\parallel = 0)$ in a QW leads to a logarithmic singularity of the Hilbert transform, $M(E_{i\Gamma_6})$ and, as a result, to a singularity of its derivative $M'(E_{i\Gamma_6} \to \epsilon_c) \to \infty$ (see Fig. 1). Then, the important parameter used to compare the contributions of the valence and conduction bands to the Bloch tail, $\psi_{b\Gamma}$ [see Eq. (10)], is the energy distance between the impurity level and the corresponding band edges. For impurities with energy levels, $E_{i\Gamma}$, that are very close to the conduction band, the contribution of the conduction band becomes dominant. For example, a vanadium impurity V^{2+} in GaAs exhibits this kind of spectrum.[41] In some cases (e.g., Cr in GaAs), the *e* state of the charged impurity may appear above the bottom of the conduction band.[15]

Therefore, similar to the case of CdS:Ni discussed in our previous paper,[24] the electron wave function, Eq. (10), can be represented as a *bonding* combination

$$\psi^{(n)}_{i\Gamma_6} = [1/\sqrt{1 + \tilde{M}'_{c\Gamma_6}}][\psi_{d\Gamma_6} + \sqrt{\tilde{M}'_{c\Gamma_6}} \psi_s]. \tag{13}$$

Thus, the Bloch tail [see Eq. (A1)] dominates in the wave function of the *n*th electron in the unfilled *d* shell of an impurity pseudoion $A^{(-)}$, and the wave function in a QW appears to be much more extended than in the bulk case. This wave function, Eq. (A5), transforms according to the irreducible representation Γ_6 and, as we shall see below, also determines the symmetry properties of the bound hole states.

IV. LOOSELY BOUND HOLE

We now calculate the hole eigenenergy, E_h, and its wave function, $\psi^{(h)}_{i\gamma}$. The second carrier in an electron-hole pair bound to a simple isoelectronic impurity is usually well described by assuming a point-charge potential. The effective-mass approximation with central-cell corrections is then applied.[42] As a result of the singularity in the mass operator, the shell of the impurity is strongly distorted due to the hybridization with the conduction-band states. Thus, the central-cell correction obtained in the QW case becomes much more important than in the bulk case.

A loosely bound state is usually orthogonalized to the core states of the impurity, which results in a contribution to the impurity potential known as a central-cell correction.[43] In the case of a bound exciton, the hole wave function is orthogonalized to the wave function of the *n*th electron. Therefore, the hole wave function takes the form

$$\psi^{(h)}_{i\gamma} = \frac{1}{\sqrt{A_\gamma}} \left[\sum_\alpha F^\gamma_\alpha \tilde{\varphi}_\alpha(\mathbf{r}) + F^{\gamma\mu}_d \psi_{i\gamma\mu} \right]. \tag{14}$$

The first term of this equation is the Bloch tail, expanded over the QW functions of the valence band, $\alpha = vj\mathbf{k}_\parallel$,

$$\tilde{\varphi}_\alpha = \varphi_\alpha - \sum_{\gamma'\mu} \langle \tilde{d}\gamma'\mu | vj\mathbf{k}_\parallel \rangle \psi_{i\gamma'\mu}, \tag{15}$$

which is orthogonalized to all states of the $A^{(-)}$ pseudoion (the γ' states include the Γ states of the outermost electron). To find coefficient $F^{\gamma\mu}_d$, the Harrison procedure is repeated for the resonance pseudopotential of noble and transition metals.[44] Inserting Eq. (14) into Eq. (6), one readily obtains

$$F^{\gamma\mu}_d = - \frac{\langle \tilde{d}\gamma | W | \psi_{b\gamma} \rangle}{E_{i\Gamma} + E_h},$$

where $W(\mathbf{r}) = U'(\mathbf{r} - \mathbf{R}_0)$ is the crystal-field potential. Factor A_γ can be determined from the normalization condition for Eq. (14). Then, in close analogy with the case of the deep resonance state,[37] we find the effective Schrödinger equation for the band part of the loosely bound hole wave function, $\psi_{b\gamma}(\mathbf{r} - \mathbf{R}_0)$;

$$\begin{aligned}&[(\hat{T} + U_0(\mathbf{r}) + V(z)) + U_c(\mathbf{r} - \mathbf{R}_0) + U_s + \hat{U}^{res}_\gamma - E_h] \\ &\quad \times \psi_{b\gamma}(\mathbf{r} - \mathbf{R}_0) = 0,\end{aligned} \tag{16}$$

where

$$\hat{U}^{res}_\gamma \psi_{b\gamma}(\mathbf{r} - \mathbf{R}_0) = \int \hat{U}^{res}_\gamma(\mathbf{r}, \mathbf{r}') \psi_{b\gamma}(\mathbf{r} - \mathbf{R}_0) d^3 r'$$

$$\hat{U}^{res}_\gamma(\mathbf{r}, \mathbf{r}') = \sum_{\gamma'} \frac{W(\mathbf{r}) | \tilde{d}\gamma' \rangle \langle \tilde{d}\gamma' | W(\mathbf{r}')}{E_{i\Gamma} + E_h}.$$

Here $U_0(\mathbf{r})$ is the periodic potential, $U_c(\mathbf{r} - \mathbf{R}_0)$ is the Coulomb potential, and $U_s = V_d(\mathbf{r} - \mathbf{R}_0) - U_h(\mathbf{r} - \mathbf{R}_0)$ is the short-range impurity potential. The resonance potential $\hat{U}^{res}_\gamma(\mathbf{r}, \mathbf{r}')$ and its role in the formation of bound excitons in the bulk case were discussed in Ref. 23.

Inserting the orthogonalized Bloch functions described by Eq. (15) into Eq. (16) leads to a system of linear equations for coefficients $F^\gamma_{vj}(\mathbf{k}_\parallel)$ that determine the wave function described by Eq. (14),

$$[E_\alpha - E_h] F^\gamma_\alpha - \sum_{\alpha'} [U^s_{\alpha\alpha'} + U^{cc}_{\gamma,\alpha\alpha'} - U^{res}_{\gamma,\alpha\alpha'}] F^\gamma_{\alpha'} = 0. \tag{17}$$

Here $U^s_{\alpha\alpha'}$ are the matrix elements of the Coulomb potential and $U^{cc}_{\gamma,\alpha\alpha'}$ and $U^{res}_{\gamma,\alpha\alpha'}$ are the short-range potential and resonance scattering potential, respectively. The states of the valence bands have different symmetries, ${}^2\Gamma_6$ (light hole) and ${}^2\Gamma_7$ (heavy hole), and are therefore decoupled, i.e., $U^s_{\alpha\alpha'} = U^s_{\alpha\alpha'} \delta_{vv'}$. It should be also taken into account that this potential is created by the charge of the exciton electron bound to the impurity with a finite localization radius. The corresponding corrections were discussed in Ref. 16, in which it was shown that it is possible to make the hole level shallower provided the radius of the swollen electron orbital $\tilde{d}\gamma$ is sufficiently different from that of the hydrogenlike bound hole. The term

$$U^{cc}_{\gamma,\alpha\alpha'} = \langle\alpha|U_s|\alpha'\rangle + S_{\alpha\gamma}(E_{i\gamma}-E_h)S^*_{\gamma\alpha'} + V_{\alpha\gamma}S^*_{\gamma\alpha'} + S_{\alpha\gamma}V^*_{\gamma\alpha} \tag{18}$$

is simply a conventional short-range impurity pseudopotential, which has a standard form, as described by Harrison.[44] Here $\langle\alpha|U_s|\alpha'\rangle = \langle\alpha|V_d(\mathbf{r}-\mathbf{R}_0)-U_h(\mathbf{r}-\mathbf{R}_0)|\alpha'\rangle$ is a matrix element of the substitutional potential that arises due to the difference between the core states of the impurity and host ion. $S_{\alpha\gamma}=\langle\alpha|\tilde{d}\gamma\rangle$ and $V_{\alpha\gamma}=\langle\alpha|W|\tilde{d}\gamma\rangle$ are the orthogonality and hybridization integrals, respectively.

Substituting the last electron wave function, Eq. (13), into Eq. (18), we obtain the contribution due to the Bloch tails of Eq. (13),

$$U^{cc}_{\Gamma,\alpha\alpha'} \approx \left(\frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}}\right) U_{d,\alpha\alpha'}, \tag{19}$$

where

$$U_{d,\alpha\alpha'} = \langle j,v\mathbf{k}_\parallel|\Delta E\hat{P}_\Gamma + W\hat{P}_\Gamma + \hat{P}_\Gamma W|j',v'\mathbf{k}'_\parallel\rangle, \tag{20}$$

$\hat{P}_\Gamma = |\varphi_\Gamma\rangle\langle\varphi_\Gamma|$ is the projection operator, φ_Γ is the Bloch tail of the impurity wave function Eq. (13), and $\Delta E = E_{i\Gamma}-E_h$. Excitons bound to TM impurities with a deep d state in a host with a T_d symmetry were studied in Ref. 16. It was found that both pseudopotential and resonance contributions are small due to the weak hybridization with the conduction-band states discussed previously. In addition, the wave function is sufficiently localized, i.e., $\tilde{M}'_{a\Gamma} < 1$, thus the term described by Eq. (18) is of no importance in the formation of the hole bound state. The bound electron charge can also be considered to be practically pointlike and its conventional effective-mass approximation, with central-cell corrections, can be used, applying Eq. (17), to describe the bound hole in the T_d bulk case.

The situation in QW (D_{2d} symmetry) appears to be quite different. The pseudopotential Eq. (18) is strongly enhanced due to the lift of the symmetry constraint for the hybridization, as discussed in the previous section, which results also in $\tilde{M}'_{a\Gamma} \gg 1$. This pseudopotential is responsible for the hole binding, whereas the Coulomb potential (decreased due to smearing of the electron charge in the center) can lead only to small corrections. It is worthwhile to compare this situation with the results of Perel' and Yassiyevich,[45] who considered the formation of deep levels by a short-range impurity potential. Although the problems are very similar, two important differences should be mentioned. The impurity potential considered by Perel' and Yassiyevich transforms according to the irreducible representation Γ_1 and does not introduce any symmetry restrictions. The structure and symmetry features of the levels created by such a potential are controlled by the host band structure. In our case, on the other hand, the impurity potential transforms according to the irreducible representation Γ_6 and has properties of the corresponding projection operator. This means that only Γ_6 band states participate in the formation of the impurity levels. As a result, our classification of the levels obtained is different than that of Perel' and Yassiyevich. The second difference is connected with the fact that Perel' and Yassiyevich considered neutral impurities, whereas we are dealing with a charged impurity. Thus, the corresponding Coulomb potential is relatively weak and may introduce only small perturbations without changing the symmetry properties of the levels. The same is true for the resonance term in Eq. (16).

The hole of the bound exciton in QW can be described as follows: (i) The short-range potential does not interact with the QW states of the topmost Γ_7 band and corresponding hydrogenlike shallow levels are formed by the Coulomb part of the impurity potential. (ii) The short-range pseudopotential splits a bound hole state from the subsequent Γ_6 bands with energies which may be essentially deeper than that of the hydrogenlike states. (iii) This level turns out to be the lowest bound hole state, and it has a smaller effective radius than that of the hydrogenlike state. Other properties of this ground state and estimates of its energy will be discussed below.

A. Hole binding energy

In the quantum well, the short-range pseudopotential described by Eq. (19) forms the bound hole states. As mentioned in the previous subsection, this potential may, therefore, form bound hole states only from the wave function of the valence band that transforms according to the Γ_6 (light-hole) representation. Thus, only one valence band can participate in the creation of bound hole states such that coefficients $F^\gamma_{\Gamma_6 j}(\mathbf{k}_\parallel)$ satisfy the equation

$$F^\gamma_{jv\Gamma_6}(\mathbf{k}_\parallel) = \frac{1}{[E_{jv\Gamma_6}(\mathbf{k}_\parallel)-E_h]}\frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}} \times \sum_{j'\mathbf{k}'_\parallel} U_{d,jj'}(\mathbf{k}_\parallel,\mathbf{k}'_\parallel)F^\gamma_{j'v\Gamma_6}(\mathbf{k}'_\parallel) = 0. \tag{21}$$

The energies of this level can be calculated using the same procedure used in our paper,[24] which takes advantage of the fact that the short-range potential of Eq. (20) contains factorizable terms. The quantities

$$A_S = \sum_{j\mathbf{k}_\parallel} S_{j\mathbf{k}_\parallel\Gamma_6}F^\gamma_{jv\Gamma_6}(\mathbf{k}_\parallel),$$

$$A_V = \sum_{j\mathbf{k}_\parallel} V_{j\mathbf{k}_\parallel\Gamma_6}F^\gamma_{jv\Gamma_6}(\mathbf{k}_\parallel), \tag{22}$$

are defined. Multiplying Eq. (21) by $S^*_{j\mathbf{k}_\parallel\Gamma_6}$ and $V^*_{j\mathbf{k}_\parallel\Gamma_6}$ and summing over $j\mathbf{k}_\parallel$ give the system of equations

$$A_S[1-B_{SS}\Delta E - B_{SV}] - A_V B_{SS} = 0,$$

$$-A_S[\Delta E B_{SV} + B_{VV}] + A_V[1-B_{SV}] = 0, \tag{23}$$

where

$$B_{SS}(E_h) = \frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}} \sum_{j,\mathbf{k}_\parallel} \frac{S^*_{j\mathbf{k}_\parallel\Gamma_6} S_{j\mathbf{k}_\parallel\Gamma_6}}{E_{vj} + \frac{(\hbar\mathbf{k}_\parallel)^2}{2m_h^*} - E_h},$$

$$B_{SV}(E_h) = \frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}} \sum_{j,\mathbf{k}_\parallel} \frac{S^*_{j\mathbf{k}_\parallel\Gamma_6} V_{j\mathbf{k}_\parallel\Gamma_6}}{E_{vj} + \frac{(\hbar\mathbf{k}_\parallel)^2}{2m_h^*} - E_h},$$

$$B_{VV}(E_h) = \frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}} \sum_{j,\mathbf{k}_\parallel} \frac{V^*_{j\mathbf{k}_\parallel\Gamma_6} V_{j\mathbf{k}_\parallel\Gamma_6}}{E_{vj} + \frac{(\hbar\mathbf{k}_\parallel)^2}{2m_h^*} - E_h}. \tag{24}$$

The summation over $\mathbf{k}_\parallel$ and the symmetry properties of the Bloch wave functions make these quantities real. The set of Eq. (23) has nonzero solutions if

$$[1 - B_{SV}(E_h)]^2 - B_{SS}(E_h)[\Delta E + B_{VV}(E_h)] = 0, \tag{25}$$

which is the equation for the hole binding energy, E_h. The simplifying approximation $V_{j\mathbf{k}_\parallel\Gamma_6} = VS_{j\mathbf{k}_\parallel\Gamma_6}$, where V is a parameter that characterizes the impurity potential, allows Eq. (25) to be rewritten in the form of

$$B_{SS}(E_h) = 1/(2V + \Delta E). \tag{26}$$

This is standard for a Koster-Slater type of problem (a graphical analysis of this kind of equation, for the case of zinc-blende semiconductors, can be found, for example, in Ref. 15). Then, Eq. (26) determines the energy of the outer exciton hole, where

$$B_{SS}(E_h) = \frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}} \sum_j \int \frac{S_{\Gamma jv}(\varepsilon)d\varepsilon}{\varepsilon - E_h} \tag{27}$$

is the conventional Hilbert transform of the local partial densities of states, $S_{\Gamma jv}(\varepsilon) = \Sigma_{\mathbf{k}_\parallel} |S_{jv\Gamma_6}|^2 \delta(\varepsilon - \varepsilon_{jv\mathbf{k}_\parallel})$. The position of the bound hole level within the forbidden energy gap is determined by the analytical properties of function $B_{SS}(E_h)$ outside the region of the allowed states in which $S_{\Gamma j}(\varepsilon) \neq 0$. $B_{SS}(E_h)$ in the allowed part of the spectrum is complex, $B_{SS}(E_h) = R_v(E_h) + i\Gamma_v(E_h)$, where the integral $R_v(E_h)$ is understood to be a principle part integral. The analytical properties of the density of the states of QW, $S_{\Gamma 1}(\varepsilon) = \frac{1}{2}\left(\frac{2m_h^*}{\hbar^2}\right)|S_{1\Gamma_6}|^2$, are reflected in the behavior of the Hilbert transform,

$$B_{SS}(E_h) = \frac{\tilde{M}'_{c\Gamma_6}}{1+\tilde{M}'_{c\Gamma_6}} \frac{1}{2}\left(\frac{2m_h^*}{\hbar^2}\right)|S_{1\Gamma_6}|^2 \ln\left|\frac{E_h + D_1}{E_h - D_1}\right|, \tag{28}$$

where $2D_1$ is the first subband width. Due to logarithmic singularities, Eq. (26) has a solution, which means that a localized level is always created in the forbidden energy gap (see Fig. 2). In the bulk case, with a wurtzite symmetry, a localized level is created only when there is a sufficiently strong scattering potential on its right-hand side. Recollecting the contribution of the electron-hole interaction to the binding energy, the results can be summarized as follows. In bulk tetrahedral semiconductors, the Coulomb potential of the bound exciton electron attracts a hole and creates a series of hydrogenlike levels, which are corrected only slightly by the short-range part of the potential. In contrast, the short-range potential of the impurity in a quantum well is relatively strong and creates a single-hole level of Γ_6 symmetry, which is corrected by the Coulomb interaction.

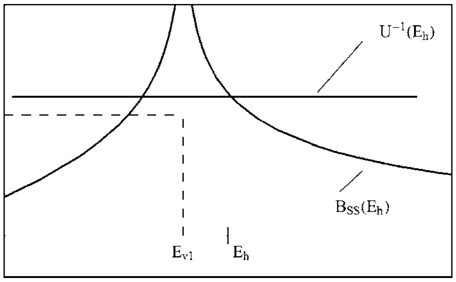

FIG. 2. Qualitative graphical solution of the Koster-Slater-type equation, Eq. (26), for the outer exciton carrier (hole) in a quantum well. The solid line shows the Hilbert transform and the dashed line shows the two-dimensional density of states. The intersection of this curve with the horizontal line representing the inverse value of the impurity potential, $U(E_h) = (2V + \Delta E)$, is shown as well.

V. EXCITON WAVE FUNCTION

Using the quasiatom model,[46] based in part on the formalism of the conventional strong crystal-field theory, the multielectron wave functions of the bound exciton become

$$\psi_\Lambda^{(ex)}(\tilde{d}^1, h) = \hat{A} \sum_{\Gamma\gamma} C^\Lambda_{\Gamma\gamma} \psi^{(n)}_{i\Gamma}(\mathbf{r}_1) \psi^{(h)}_{i\gamma}(\mathbf{r}_2).$$

Here $C^\Lambda_{\Gamma\gamma}$ are the Clebsch-Gordan coefficients realizing the direct product Λ of the multielectron wave functions that correspond to the irreducible representations, Γ, of the electron and the loosely bound γ hole. $\hat{A}$ is the antisymmetrization operator, here $\Gamma, \gamma = \Gamma_6$. The electron wave function, $\psi^{(n)}_{i\Gamma}(\mathbf{r}_1)$, is given by Eq. (13) and the normalized hole wave function, Eq. (14), takes the form [cf. Eq. (31) in Ref. 24]

$$\psi^{(h)}_{i\Gamma_6} = \frac{1}{\sqrt{1 + |F_d^\Gamma|^2}} \times \left[\frac{1}{\sqrt{\tilde{M}'_{v\Gamma_6}}} \sum_{j,\mathbf{k}_\parallel} \frac{S_{j\mathbf{k}_\parallel\Gamma_6}}{E_{vj} + \frac{(\hbar\mathbf{k}_\parallel)^2}{2m_h^*} - E_h} \tilde{\varphi}_\alpha(\mathbf{r}) + F_d^\Gamma \psi_{i\Gamma} \right]. \tag{29}$$

We see that the hole wave function has acquired a core part, denoted by subscript d, which results from the resonance mechanism. Thus, the hole state has a structure similar to that of its electron counterpart, Eq. (13), in the bound exciton state. The contributions of the Bloch tail to the electron wave function, Eq. (13), and of the d core to the hole wave function are controlled by coefficients $\tilde{M}'_{c\Gamma_6}$ and $|F_d^\Gamma|^2$, respectively. If special reasons exist for the enhancement of these coefficients, then "equalization" of the above-mentioned electron and hole wave functions can occur. It can now be seen that swelling of the electron component (large $\widetilde{M}'_{c\Gamma_6}$, Fig. 1) results in strong orthogonalization corrections to the hole wave function (large $|F_d^{\Gamma}|^2$), and the ultimate source of these two effects is the anomalously strong hybridization of the $d\Gamma_6$ states with the conduction-band states of the same symmetry. Such behavior is consistent with a quenching of the orbital angular momentum of the loosely bound hole in the short-range potential, which causes it to behave like a pure spin $\frac{1}{2}$ particle.

The various exciton wave functions transform according to the irreducible representation $\Gamma^{(ex)}=\Gamma^{(de)}\times\Gamma^{(h)}$, which is merely a direct product of the electron and hole representations. The hole representation, $\Gamma^{(h)}=\Gamma^{(vb)}\times\Gamma^{(env)}$, is the product of the valence bands, $\Gamma^{(vb)}$, and the hydrogenlike envelop functions, $\Gamma^{(env)}$. Therefore, patterns obtained for standard bound excitons in TM impurities are known for their rich and complicated structure. Here, in the case of IBE, the state of the hole is formed by the short-range pseudopotential Eq. (18) with the projection operator $\hat{P}_{\Gamma_6}$ built in. Thus, its wave functions transform according to representation Γ_6. The Γ_6 of the impurity d electron gives $\Gamma^{(ex)}=\Gamma_6\times\Gamma_6=\Gamma_1+\Gamma_2+\Gamma_5$ representation for the exciton bound states. The exchange interaction splits this level into a singlet, Γ_1, and a triplet, $\Gamma_2+\Gamma_5$.

The electron-hole wave functions of the IBE are characterized by their intermediate radius of localization. Hence, the electron hole's overlapping wave function of IBE becomes much greater than that of standard bound excitons. As a result, the exciton recombination is enhanced (cf. the antenna effect considered by Rashba and Gurgenishvili[47]). The enhanced overlapping may also increase the electron-hole exchange interaction. The electron-hole scattering via the exchange scattering may give rise to spin relaxation by the so-called Bir Aronov-Pikus (BAP) process.[48] Since the electron-hole pair is bound by selective short-range pseudopotentials that attract only light holes with Γ_6 symmetry, mixing of light and heavy holes is not allowed. On the other hand, the long-range Coulomb potential, which allows mixing of different hole states and is effective for the BAP process,[49] is weak in the IBE. Therefore, the spin relaxation of the BAP process is not effective for IBE in QW of III-V elements.

CONCLUSION

We found that there are reasons for introducing the intermediately bound exciton concept in the case of a QW. We have also seen that the difference between the bound exciton states in the zinc blende, T_d, bulk case and the QW case is due primarily to the lower D_{2d} symmetry of the latter. It is also important to note that only when the relevant impurity deep level is close enough to the bottom of the conduction band does the enhancement of the *d-s* hybridization play a truly important part. The structures of the bound exciton wave functions in the two cases are strongly at variance. The bulk case is characterized by standard excitons that are bound to the TM impurity as described, for instance, in review.[23] The electron is bound in a strongly localized d state described by an *antibonding superposition*, while the hole is loosely bound by the Coulomb field of the electron.

The QW case is characterized by an IBE in which the first carrier is also bound rather loosely due to a strong hybridization of the d states with the states at the bottom of the conduction band. This is described by a *bonding superposition* with a higher-lying QW subband of the conduction band states. This hybridization of the impurity d states with conduction-band states leads to a symmetry that is forbidden in the bulk case but is allowed in the lower-symmetry QW. As an example, we examined the D_{2d} symmetry with an acceptor exciton and showed that the wave function of the nth electron of the $A^{(-)}$ pseudoion is significantly swollen due to the hybridization of the d states with the Bloch states at the bottom of the QW subband in the conduction band. The dominant potential responsible for binding the outer carrier (hole) is a short-range pseudopotential with properties of a projection operator projecting onto the Γ_6 subspace. This potential is therefore capable of binding only light holes from the valence bands of Γ_6 symmetry. Unlike the conventional binding scheme of the second carrier with a hydrogenlike excited-state spectrum, only one energy state of the Koster-Slater type is expected here, which might be deeper.

There are various consequences of this model that can be examined experimentally. An important manifestation of the differences between IBE and DBE is completely different values of the exciton g factors, which reflect the different localizations and symmetries of the exciton wave functions. We should also mention the shift of the IBE's binding energy, as well as some other physical properties of these systems.

APPENDIX: THE ELECTRON PART

Here the Bloch tail of the impurity wave function Eq. (13) is calculated according to

$$\sqrt{\widetilde{M}'_{c\Gamma_6}}\psi_{b\Gamma}=\sum_{cj\mathbf{k}_\parallel}\frac{\langle d\Gamma_6|U'(\mathbf{r}-\mathbf{R}_0)|c\widetilde{j\mathbf{k}_\parallel}\rangle}{\left(E_{cj}+\dfrac{(\hbar\mathbf{k}_\parallel)^2}{2m_h^*}\right)-E_{i\Gamma}}\widetilde{\varphi}_{cj\mathbf{k}_\parallel}, \qquad \text{(A1)}$$

assuming that the main contribution is from the vicinity of the Γ point of the conduction band, thus allowing the use of the following approximation. It is assumed that the hybridization with the conduction band, $\widetilde{V}_{cj\Gamma}$, is $\langle d\Gamma_6|U'(\mathbf{r}-\mathbf{R}_0)|c\widetilde{j\mathbf{k}_\parallel}\rangle\approx\widetilde{V}_{cj\Gamma_6}$. The basis of the orthogonalized Bloch functions, $\widetilde{\varphi}_{cj\mathbf{k}_\parallel}$, is substituted by the set of Kohn-Luttinger functions

$$\widetilde{\varphi}_{cj\mathbf{k}_\parallel}=\widetilde{u}_{0cj}e^{-\mathbf{k}_\parallel\cdot\boldsymbol{\rho}}$$

with the Bloch amplitude at $k_\parallel=0$

$$\widetilde{u}_{0cj}(\boldsymbol{\rho},z)=u_{0c}(\boldsymbol{\rho})\chi_j(z)-\sum_{\gamma\mu}\langle\psi_{\gamma\mu}|u_{0c}(\boldsymbol{\rho})\chi_j(z)\rangle\psi_{\gamma\mu}$$

orthogonalized to the core states. As a result, the tail wave function becomes

$$\sqrt{\widetilde{M}'_{c\Gamma_6}}\psi_{b\Gamma} \simeq \sum_{cj\mathbf{k}_\parallel} \widetilde{V}_{cj\Gamma} \frac{e^{-\mathbf{k}_\parallel \cdot \boldsymbol{\rho}}}{|E_{cj}-E_{i\Gamma}| + \frac{(\hbar \mathbf{k}_\parallel)^2}{2m_e^*}} \widetilde{u}_{0cj}(\boldsymbol{\rho},z). \tag{A2}$$

Replacing the summation over $k_\parallel$ with integration for the two-dimensional case yields

$$\sqrt{\widetilde{M}'_{c\Gamma_6}}\psi_{b\Gamma} \simeq \left(\frac{1}{2\pi}\right)^2 \frac{2m_e^*}{\hbar^2} \sum_j \widetilde{V}_{cj\Gamma}\widetilde{u}_{0cj}(\boldsymbol{\rho},z) \times \int^{\infty 2\pi}\int_{00} \frac{e^{-k_\parallel \rho \cos\theta} k_\parallel dk_\parallel d\theta}{k_{\Gamma cj}^2 + k_\parallel^2}, \tag{A3}$$

where $k_{\Gamma cj}^2 = \frac{2m_e^*}{\hbar^2}\Delta_{cj\Gamma}$ and $\Delta_{cj\Gamma} = |E_{cj}-E_{i\Gamma}|$. By expanding the plane wave in the cylindrical component using the Bessel function of the first kind, $J_0(k_\parallel \rho)$, and performing the angular integral and the integral over $k_\parallel$, the tail wave function becomes

$$\sqrt{\widetilde{M}'_{c\Gamma_6}}\psi_{b\Gamma} \simeq \left(\frac{1}{2\pi}\right)^2 \frac{2m_e^*}{\hbar^2} \sum_j \widetilde{V}_{cj\Gamma}\widetilde{u}_{0cj}(\boldsymbol{\rho},z) 2\pi K_0(k_{\Gamma cj}\rho), \tag{A4}$$

where $K_0(k_{\Gamma cj}\rho)$ is the modified Bessel function. The normalized wave function of this tail part can be presented as

$$\sqrt{\widetilde{M}'_{c\Gamma_6}}\psi_{b\Gamma} \simeq \sum_j \frac{\widetilde{V}_{cj\Gamma}}{\Delta_{cj\Gamma}} \varphi_{cj}(z,\rho), \tag{A5}$$

$$\varphi_{cj}(z,\rho) = \left(\int |\widetilde{u}_{0cj}(\boldsymbol{\rho},z) K_0(k_{\Gamma cj}\rho)|^2 d^3 r\right)^{-1/2} \times \widetilde{u}_{0cj}(\boldsymbol{\rho},z) K_0(k_{\Gamma cj}\rho). \tag{A6}$$

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