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Splitting of the energy spectrum of an indirect exciton upon electron tunnelling between nanoparticles

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Abstract. **We report an analytical study of the splitting of the energy spectrum of an electron for a quasi-two-dimensional indirect exciton (Q2D-IX) localised at the 'dielectric nanoparticle–dielectric medium' interface. The splitting results from electron tunnelling through a potential barrier separating neighbouring nanoparticles. The obtained expressions determine the energy and spatial parameters of the probability of electron tunnelling and the value of the energy splitting. It is found that tunnelling is possible under rigid conditions for the spatial parameters of the nanosystem and the ratio of the energies of the excited and ground exciton states. Tunnelling-induced splitting of the electron energy can reach 0.1 eV for some dielectric structures. This allows the impact of charge tunnelling on the energy spectrum of Q2D-IX systems to be predicted.**

Keywords: *indirect excitons, tunnelling, energy splitting, heterostructures.*

1. Introduction

Excitons largely determine the optical and optoelectronic properties of low-dimensional dielectric and semiconductor structures. This is especially pronounced for 2D materials [1], which have a huge potential for practical application. The appearance of van der Waals heterostructures [2] made it possible to experimentally record the physical properties caused by indirect excitons (IXs) at room temperature [3, 4].

A small overlap of the wave functions of an electron and a hole, as well as a low dielectric screening, leads to the formation of strongly coupled and long-lived IXs upon optical excitation [2, 5–12]. Some studies demonstrate a more pronounced manifestation of IXs in the photoluminescence spectra in comparison with interlayer excitons [2, 6, 8, 9]. This is largely due to the processes of interlayer tunnelling of exciton-bound charge carriers [8].

Theoretical studies show the possibility of forming an IX in nanosystems based on dielectric nanoparticles (NPs) in a dielectric matrix [13–15]. In this case, an electron and a hole are localised in a thin surface layer on different sides of the nanoparticle–matrix interface. As a result of these studies, a strong dependence was found between the NP size and the IX energy, i.e. with an increase in the NP radius, the energy of the stationary state of the exciton tends to the 2D-IX energy in a layer with a permittivity $\tilde{\varepsilon} = 2\varepsilon_1\varepsilon_2/(\varepsilon_1 + \varepsilon_2)$, where ε_1 and ε_2 are permittivities of NPs and the matrix, respectively [15]. Such an exciton is a quasi-two-dimensional indirect exciton (Q2D-IX), since its centre of mass can move along the curved NP surface in three coordinates, in contrast to a 2D-IX. An estimate of the Q2D-IX bond energy shows that it can be two orders of magnitude higher than the value corresponding to a bulk material [14, 15]. As a consequence, this leads to a long lifetime and a spin relaxation time, and also makes it possible to study high-temperature quantum Bose gases and create exciton devices operating at room temperature [16–19].

An interesting feature is also the formation of chains and superlattices from interacting Q2D-IXs with an energy spectrum tuned by changing the NP size. The spatial structure of these Q2D-IX systems can affect their optical and optoelectronic properties, similar to multilayer nanoheterostructures [19, 20]. Some of these properties may be due to the tunnelling of charge carriers that make up an exciton through the spatial and energy barriers between excitons in neighbouring NPs. This problem has not yet been sufficiently studied, despite the fact that tunnelling of charges between NPs has been known for more than twenty years [21–24].

In this work, using the Wenzel–Kramers–Brillouin (WKB) approximation [25], we analytically study and numerically simulate the effect of electron tunnelling in a Q2D-IX on the splitting of its energy spectrum. These electrons reside in a dielectric medium between two NPs. The potential barrier separating the electrons in a Q2D-IX is formed by the Coulomb field of exciton holes localised in the near-surface layer of a neighbouring NP. Analytical expressions are obtained for the splitting of the energy spectrum of electrons, and the spatial and energy parameters for the possibility of tunnelling are estimated. The expressions obtained are also applicable to IXs of layered dielectric nanoheterostructures.

As a result of the splitting of energy states in the band gap of the matrix, there arises a localised band of electronic states, which ensures the tunnelling of electrons in a Q2D-IX and an increase in the photoconductivity of the nanosystem. We believe that the presented results will be useful both for theoreticians and experimenters working in the field of solid state physics, materials science, optics and physics of nanostructures, optoelectronics, excitonics, and spectroscopy.

2. Splitting of electron energy

Let us consider the states of Q2D-IX electrons localised in a medium as states of electrons in potential wells $U_0(x)$ formed by holes in corresponding dielectric NPs and by the potential of the nanoparticle–medium interface (Fig. 1). In addition to

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a spatial barrier with a width of $2d$, equal to the distance between the centres of mass of Q2D-IXs, these electrons are separated by a potential barrier U. The absence of electron tunnelling through these barriers would lead to the existence of exciton energy levels corresponding to an electron localised only in one of the potential wells. Otherwise, the electron wave function e_1 will be nonzero in the vicinity of NP2. This leads to the splitting of each electronic energy state in a Q2D-IX (NP1), with exciton states also splitting, which follows from the expression

$$E_{ex} = E_g - E_e + E_k, \tag{1}$$

where E_g is the bandgap energy of the medium where the exciton is localised; E_e is the Q2D-IX binding energy (the electron energy in the potential well); and E_k is the kinetic energy of the exciton.

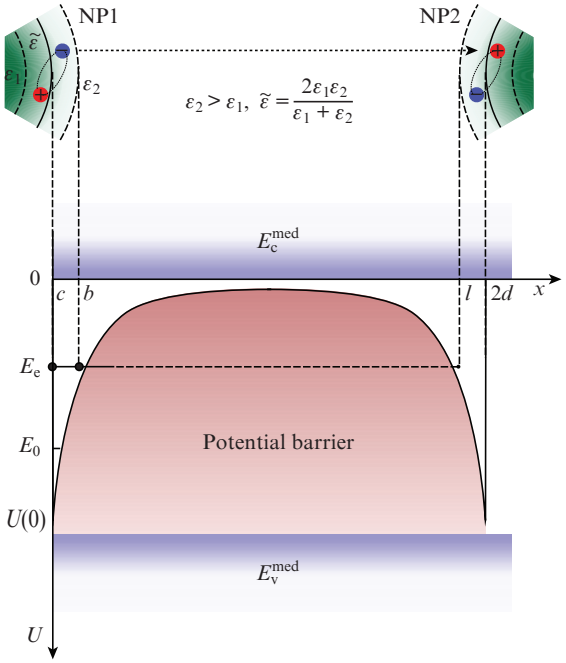

Figure 1. System of two Q2D-IXs separated by a potential barrier.

The potential barrier U for electron e_1 separating two neighbouring potential wells is formed by Coulomb potentials U_1, U_2, and U_3 of the interaction of electron e_1 with holes NP1, NP2 and electron e_2, respectively, and the centrifugal potential of the electron motion in the Coulomb field of the hole. If electrons e_1 and e_2 with effective masses m_e are localised above the NP surface in a medium with permittivity ε_2, holes with effective masses m_h are localised in NPs with permittivity ε_1, then the ratios of potentials U_3 to U_1 and U_2 are proportional to $2\varepsilon_2/(\varepsilon_2 + \varepsilon_1)$ and are small when $\varepsilon_1 < \varepsilon_2$. The centrifugal potential is comparable to the value of the Coulomb interaction energy at distances of the Bohr radius of the exciton, a_{ex}, and decreases with increasing distance d in proportion to $1/d^2$. Thus, its contribution is insignificant at $2d \gg a_{ex}$, which also satisfies the conditions of the semi-classical approximation in the Coulomb field [24]. If the potential of the well is measured from the bottom of the conduction band, then the electron energy in this well will be equal to the electron binding energy in the exciton, E_e. The depth of the potential well for a single NP is equal to the Q2D-IX binding energy in the ground state E_0. With a large NP radius, this energy tends to the 2D-IX energy value [15, 26]:

$$E_{2D} = -\frac{2\hbar^2}{m_{ex}a_{2D}^2} = -\frac{2e^4 m_{ex}}{\tilde{\varepsilon}^2\hbar^2}, \tag{2}$$

where $a_{2D} = \tilde{\varepsilon}\hbar^2/(2e^2 m_{ex})$ is the Bohr radius of a 2D-IX; $m_{ex} = m_e m_h/(m_e + m_h)$ is the 2D-IX reduced mass; $\tilde{\varepsilon} = 8\pi\varepsilon_0\varepsilon_1\varepsilon_2/(\varepsilon_1 + \varepsilon_2)$ is the effective static permittivity of the near-surface layer in which a 2D-IX is localised. Taking into account that a Q2D-IX is localised almost on the NP surface, in a layer of thickness a_{ex}, we can determine the distance $2d$ between the NP surfaces, which is the distance between the centres of mass of excitons. In the coordinate system shown in Fig. 1, the potential barrier of electron e_1 at a distance of $0 \leqslant x \leqslant 2d$ is determined by the expression:

$$U(x) = U_1(x) + U_2(x)$$

$$= \frac{E_0 a_{ex}}{a_{ex} + x} + \frac{E_0 a_{ex}}{a_{ex} + 2d - x}. \tag{3}$$

The height of this barrier for the lowest energy electron corresponding to the Q2D-IX ground state is

$$|U(0)| = \left| E_0 + \frac{E_0 a_{ex}}{(a_{ex} + 2d)} \right|. \tag{4}$$

This is higher than the energy E_0 of the 2D-IX ground state in the case of a single NP. In accordance with the WKB approximation, the splitting of the excited energy state E_e can be written in the form [25]

$$\Delta E = \frac{2\hbar\omega}{\pi} \exp\left[-(1/\hbar) \int_b^l |p(x)| \mathrm{d}x \right], \tag{5}$$

where

$$|p(x)| = \left| \sqrt{2m_e \left[|U(x)| - |E_e| \right]} \right| \tag{6}$$

is the momentum of the electron inside the potential well; and

$$\omega = \pi / \int_c^b \frac{\mathrm{d}x}{\sqrt{\frac{2}{m_e}\left[|U_0(x)| - |E_e| \right]}} \tag{7}$$

is the frequency of the classical periodic motion of an electron in a potential well $U_0(x)$. Coordinates c, b and l are found from the conditions

$$U_0(c) = E_e,\ U(b) = U(l) = E_e. \tag{8}$$

An electron in a Q2D-IX is localised in the layer $b \geqslant x \geqslant 0$ and, therefore, $c = 0$. The potential of the NP–medium interface is a complex superposition of Coulomb charge fields on the surface and their images, and its explicit form is unknown. Thus, we cannot use the expression for the

Hamiltonian of the electron in the potential $U_0(x)$ to determine the energy E_e using the Schrödinger equation. Therefore, to calculate the integrals in (5) and (7), we use the virial theorem [27–29]

$$\langle |U_0(x)| \rangle = \frac{2}{k+2}|E_e|, \tag{9}$$

and for $k = -1$ we obtain

$$\omega = \frac{\pi}{b}\sqrt{\frac{2|E_e|}{m_e}}. \tag{10}$$

Similarly, using the virial theorem inside the potential well

$$|E_e| = \frac{1}{2}|U_0(x)|, \tag{11}$$

we have

$$\int_b^l |p(x)|\mathrm{d}x = \int_b^l \sqrt{m_e\left|\frac{E_0 a_{ex}}{(a_{ex}+x)} + \frac{E_0 a_{ex}}{(a_{ex}+2d-x)}\right|}\mathrm{d}x. \tag{12}$$

The limits of integration can be determined from (8):

$$b = d - (a_{ex}+d)\sqrt{1 - \frac{E_0 a_{ex}}{(a_{ex}+d)E_e}},$$
$$l = d + (a_{ex}+d)\sqrt{1 - \frac{E_0 a_{ex}}{(a_{ex}+d)E_e}}. \tag{13}$$

After integrating (12), we find

$$\int_b^l |p(x)|\mathrm{d}x = 2\sqrt{2m_e|E_0|a_{ex}(a_{ex}+d)} \times \arcsin\sqrt{1 - \frac{a_{ex}}{(a_{ex}+d)}\frac{E_0}{E_e}}. \tag{14}$$

Using (5), (10), and (14), we can obtain an expression for the magnitude of the splitting of the exciton state caused by electron tunnelling between Q2D-IXs:

$$\Delta E = \frac{2\hbar}{b}\sqrt{\frac{2|E_e|}{m_e}} \times \exp\left[W \arcsin\sqrt{1 - \frac{a_{ex}}{(a_{ex}+d)}\frac{E_0}{E_e}}\right], \tag{15}$$

where $W = -2\sqrt{2m_e|E_0|a_{ex}(a_{ex}+d)}/\hbar$.

Figure 2 shows the result of estimating the energy splitting using (15) for SiO_2 (NPs) – Si (medium) (the corresponding parameters are given in Table 1).

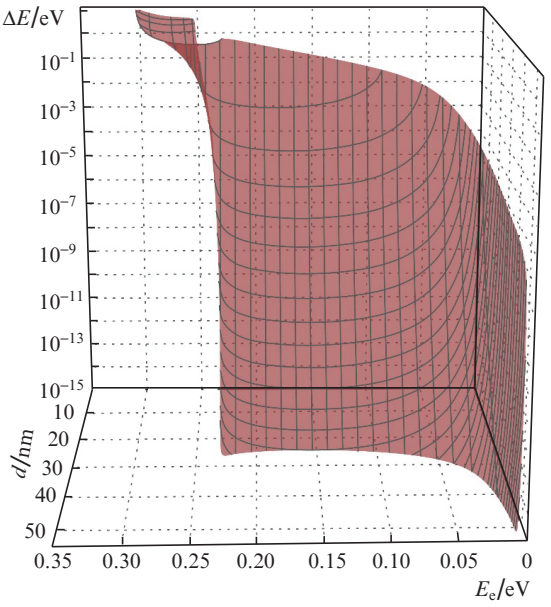

Figure 2. 3D surface of energy splitting ΔE as a function of half the distance d between nanoparticles and the energy E_e of the excited state in the case of a SiO_2 NP–Si medium.

Table 1. Materials and parameters for evaluating the splitting ΔE (m_0 is the mass of a free electron).

Material	m_h/m_0	m_e/m_0	$\varepsilon/\varepsilon_0$
SiO_2	0.4 [30]		3.9 [31]
Si		1.06 [32]	12 [33]
Si_3N_4	2.9 [34]	1.6 [34]	7.4 [33]
ZnO	0.45 [35]		3.7 [35]
TiO_2		10 [35]	174 [35]

3. Calculation results and discussion

As mentioned above, the framework of the semi-classical approximation in the Coulomb field is limited by distances larger than the radius of the first Bohr orbital. For the practical use of expression (15), it is useful to know the ranges of energies E_0, E_e and the spatial dimensions of the nanosystem, which satisfy the condition of applicability of the WKB approximation. For a Q2D-IX, the energy spectrum can differ significantly from the hydrogen-like spectrum [17] and depend on the size of the NP and the curvature of its surface. Based on the condition $|E_e| \leqslant |E_0|$ and taking into account that b and l take real values and $b \geqslant 0$, we obtain

$$\frac{a_{ex}+d}{a_{ex}+2d}|E_0| \geqslant |E_e| \geqslant \frac{a_{ex}}{a_{ex}+d}|E_0|, \tag{16}$$

$$\frac{a_{ex}}{a_{ex}+d} \leqslant 1. \tag{17}$$

Using expression (12) and the condition of applicability of the WKB approximation $|\hbar \mathrm{d}[p(x)]^{-1}/\mathrm{d}x| \ll 1$, we find for E_0 on the interval $2d \geqslant x \geqslant 0$:

$$|E_0| \gg \max\left|\frac{4\pi^2\hbar^2(x-d)^2}{2(a_{ex}+d)m_e a_{ex}(-x^2+2xd+a_{ex}^2+2a_{ex}d)}\right|. \tag{18}$$

Inequalities (16), (17), and (18) determine the range of electron binding energies in Q2D-IXs, the depth of the potential well, and the size of the nanosystem for which electron tunnelling is possible. It should be noted that in the framework of this work, we consider both Q2D-IXs as independent quantum systems. But for small distances between excitons ($2d < \hbar/\sqrt{6|E_e|m_e}$), when the wave functions of the electrons overlap, tunnelling is possible if the quantum states of the Q2D-IX electrons are different.

Let us consider the case of a large NP radius, when the Q2D-IX states tend to the 2D-IX states. The highly excited states of this exciton satisfy the conditions $[a_{2D}/(a_{2D} + d)]E_0 \approx E_e$, $b \approx d$, and we can write expression (15) as

$$\Delta E_{he} \approx \frac{2\hbar}{d}\sqrt{\frac{2a_{2D}|E_0|}{(2a_{2D}+d)m_e}}$$

$$= \frac{2e\hbar}{d}\sqrt{\frac{2}{(2a_{2D}+d)\tilde{\varepsilon}m_e}}. \quad (19)$$

For low-excited Q2D-IX levels, as follows from (16), $|E_0| \geqslant 2|E_e|$, and for $d \gg a_{2D}$,

$$\arcsin\sqrt{1-2\frac{a_{2D}}{a_{2D}+d}} \approx \frac{\pi}{2}, \quad b \approx \frac{a_{2D}^2}{d}$$

the expression for the splitting of the energy takes the form

$$\Delta E_{le} \approx \frac{2d\hbar}{a_{2D}}\sqrt{\frac{e^2}{\tilde{\varepsilon}m_e a_{2D}^2}}$$

$$\times\exp\left[-\frac{\pi e}{\hbar}\sqrt{\frac{2m_e}{\tilde{\varepsilon}}(a_{2D}+d)}\right]. \quad (20)$$

To estimate the magnitude of the energy splitting taking into account (19) and (20), we use the data in Table 1. The evaluation results are shown in Fig. 3. One can see that the splitting of highly excited states, in contrast to low excited ones, is significant even at a distance of tens of nanometres between NPs and has a less pronounced dependence on the materials of the medium and nanoparticles.

4. Conclusions

The presented theoretical analysis shows that tunnelling of charge carriers between Q2D excitons in the NP superlattice is possible if relations (16), (17), and (18) are satisfied for the spatial parameters of the superlattice and the energy spectrum of excitons. As a result of tunnelling, the energy spectrum of electrons is broadened, and a band of electronic states is formed. This band will be in the energy gap E_g if the height of the potential barrier is lower than E_g or, in other words, the distance $2d$ satisfies the condition $2d > [(2E_g - |E_0|)/(E_g - |E_0|)]a_{ex}$. The magnitude of the energy splitting depends on the exciton binding energy, effective masses of charge carriers, permittivity of the surface layer, and the distance between NPs. The contribution of these parameters is different for each value of the energy of the exciton state. For excited states with $|E_e| \ll |E_0|$

$$\Delta E_{ex} \sim \frac{1}{\tilde{\varepsilon}}\left(\frac{1}{d}\right)^{3/2}\left(\frac{m_{ex}}{m_e}\right)^{1/2}. \quad (21)$$

For states close to the ground ones with $E_e \sim E_0$

$$\Delta E_{gr} \sim \frac{dm_{ex}^2}{\tilde{\varepsilon}^3}\sqrt{\frac{m_{ex}}{m_e}}\exp\left(-\sqrt{\frac{m_e}{\tilde{\varepsilon}}}d\right). \quad (22)$$

All of the above can affect the energy spectrum of a Q2D-IX, as well as the structure of the forbidden and valence bands of the medium. The formation of an allowed energy band with an adjustable width is useful for increasing the tunnelling photoconductivity; therefore, the results obtained can be applied in the field of exciton physics, instrumentation, nanotechnology, and materials science, where excitons and nanoparticles are in demand as one of the main elements that determine the desired properties.

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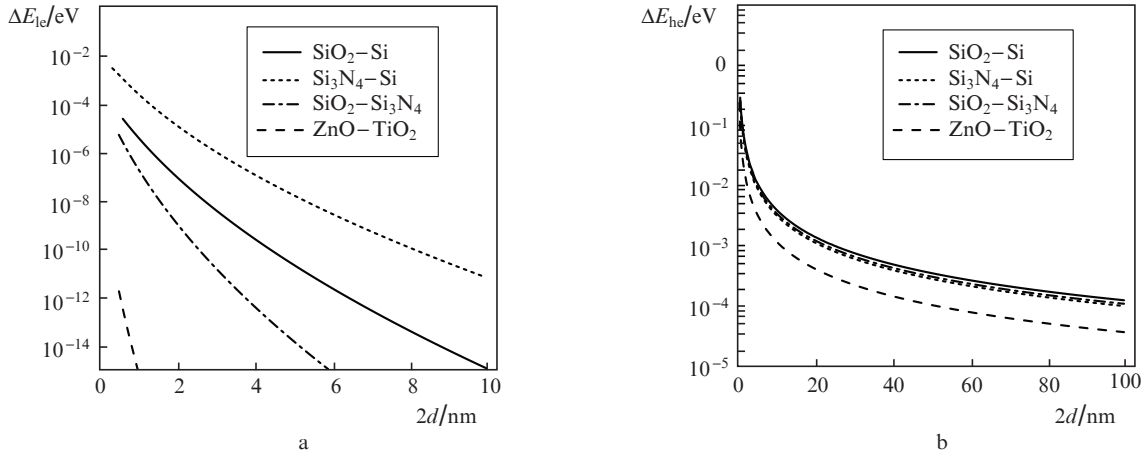

Figure 3. Splitting of energy as a function of the distance between nanoparticles for various NP–medium materials, estimated using expressions (20) and (19) for (a) low-excited and (b) high-excited states, respectively.

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