Optical properties of quazi-zero dimensional structures with two-electron impurity centers

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Abstract. A generalization of the zero-radius potential (ZRP) method in case of two-electron impurity centers in quantum dots with zero nuclear charge was made in this work. As a part of the semi-empirical model of the variational method, there was obtained an analytical equation for the first ionization potential of the two-electron impurity center. In the dipole approximation, the coefficient of impurity absorption of light at the two-electron double ionization of impurity centers in case of quantum dots synthesized in a transparent dielectric matrix is calculated.

1. Introduction

A large number of impurities in semiconductors in bound state may have not one, but two electrons, therefore behave like helium-like impurity centers. The difficulty of theoretical study of two-electron impurity states are due to the complex nature of the interaction of electrons in the outer shell of the impurity center with the valence electrons of the nearest lattice atoms [1]. As a result, it is impossible to predict not only the position of multicharge levels, but also their possible charge states. Of particular interest is the process of double photoionization of two-electron impurity centers with a single photon. This reaction is one of the fundamental reactions involving multiple particles. Theoretical approaches to the study of such reactions are developed in works [2, 3]. The purpose of this work is to calculate the first ionization potential of a two-electron impurity center in a quantum dot (QD) by using the variation method, and to study theoretically the features of double photoionization of two-electron impurity centers in a quazi-zero dimensional structure which is a dielectric matrix with synthesized QDs.

2. The energy spectrum of a two-electron impurity center in a semiconductor QD

Let’s consider a semi-empirical model of two-electron impurity centers in QDs. Short-range potential in this model is approximated by a potential well of depth $V_0$, radius of which $d$ is much smaller than the radius of the localized state. As an empirical parameter, we take the energy of doubly ionized impurity, i.e., the second ionization potential, $E_2$. Thus, the task is to calculate the first ionization potential, $E_1$, the value of which can be calculated by the Ritz variation method. The chosen units of length and energy are, respectively, $a_d = e\hbar^2/m^*e^2$ – the effective Bohr radius and $E_d = \hbar^2/2m^*a_d^2$ – the effective Bohr energy. At the same time, it is recognized that the power of short-range potential,
$V_0 d^2$ in case of $d \to 0$ remains finite. The two-electron wave function $\Psi(\rho_1, \rho_2)$ satisfies the Schrödinger equation

$$H(\rho_1, \rho_2)\Psi(\rho_1, \rho_2) = E\Psi(\rho_1, \rho_2),$$  \hspace{1cm} (1)

where $H(\rho_1, \rho_2) = H(\rho_1) + H(\rho_2) + \frac{\hbar^2}{m^* a_d^2} |\rho_1 - \rho_2|$, $H(\rho_i) = -\frac{\hbar^2}{2m^* a_d^2} \Delta_i - \frac{\hbar^2}{2m^* a_d^2} V(\rho_i)$, $\rho_d = d/a_d$,

$$V(\rho_i) = \begin{cases} V_0^*, & \rho_i \leq \rho_d, \\ 0, & \rho_i > \rho_d, \end{cases} \quad V_0^* = V_0 / E_d, \quad \rho_i = r_i / a_d, \quad r_i – \text{coordinates of electrons in case of } i=1,2, m^* – \text{the effective mass of electron.}

Usually, the simplest form of the two-electron wave function $\Psi(\rho_1, \rho_2)$ leading to a satisfactory approximation in helium-like centers is the product of one-electron wave functions.

$$\Psi(\rho_1, \rho_2) = \Psi(\rho_1)\Psi(\rho_2),$$  \hspace{1cm} (2)

Using the results of [4], in the model of a spherically symmetrical potential well (the “hard walls” model), an equation for the wave function of an electron localized on the short-range potential in a QD $\Psi(\rho_i)$ is:

$$\Psi(\rho_i) = \frac{B}{\rho_i} \begin{cases} \frac{\sinh(R_0^* \eta^{-1} - \rho_i \eta^{-1}) \sin(\chi_0 \rho_i)}{\sinh(R_0^* \eta^{-1})} \sin(\chi_0 \rho_d), & \rho_i \leq \rho_d \\ \frac{\sinh(R_0^* \eta^{-1} - \rho_i \eta^{-1})}{\sinh(R_0^* \eta^{-1})}, & \rho_i \geq \rho_d \end{cases},$$  \hspace{1cm} (3)

where $\chi_0 = \sqrt{V_0^* - \eta^{-2}}$, $V_0^* = V_0 / E_d$, $\eta = \sqrt{E_d / E_2}$, $R_0^* = R_0 / a_d$, $R_0$ – the QD radius, $B = \sqrt{2 \eta^{-1} \left( \tanh(R_0^* \eta^{-1}) - R_0^* \eta^{-1} \tfrac{\csc(2R_0^* \eta^{-1})}{\csc(2R_0 \eta^{-1})} \right)}$.

In view of (3), the trial two-electron wave function can be written as:

$$\Psi(\rho_1, \rho_2) = \frac{B^2}{\rho_1 \rho_2} \begin{cases} \frac{\sin^2(\chi_0 \rho_i) \sin(\chi_0 \rho_2)}{\sin^2(\chi_0 \rho_i)} \sin(\chi_0 \rho_d), & \rho_i \leq \rho_d \\ \frac{\sinh^2(R_0^* \eta^{-1} - \rho_i \eta^{-1}) \sin(\chi_0 \rho_2)}{\sinh^2(R_0^* \eta^{-1})}, & \rho_i \geq \rho_d \end{cases},$$  \hspace{1cm} (4)

The energy of a two-electron impurity center is determined by the minimum average value of the Hamiltonian $\varepsilon(R_0^*, \eta)$:

$$\varepsilon(R_0^*, \eta) = E_d \left\langle \Psi(\rho_1, \rho_2) | H(\rho_1, \rho_2) | \Psi(\rho_1, \rho_2) \right\rangle / \left\langle \Psi(\rho_1, \rho_2) \right\rangle^2.$$  \hspace{1cm} (5)

Making a limit pass ($d \to 0$) for $\varepsilon(R_0^*, \eta)$, the result is:
\[ \varepsilon(R_0^*, \eta) = -\frac{2^\eta \pi^2 E_d}{\text{sh}^4 (R_0^* \eta^{-1}) \left( \text{th}(R_0^* \eta^{-1}) - R_0^* \eta^{-1} \csc \left( R_0^* \eta^{-1} \right) \right)^2} \times \]
\[ \times \left( 2^{-\eta} \left( \text{sh} \left( 2 R_0^* \eta^{-1} \right) - \text{sh} \left( 2 \eta^{-1} R_0^* \right) \right)^2 + \eta^{-1} \right) \times \]
\[ \times \left( -4 \eta^{-1} R_0^* - 8 \text{ch} \left( \eta^{-1} R_0^* \right) \text{sh} \left( \eta^{-1} R_0^* \right) \text{Chi} \left( 2 \eta^{-1} R_0^* \right) + 2 \ln \left( 2 \exp(1 + C) \eta^{-1} R_0^* \right) \right) \times \]
\[ \times \left( \text{sh} \left( 2 \eta^{-1} R_0^* \right) + (\text{Chi} \left( 4 \eta^{-1} R_0^* \right) - \ln(2)) \text{sh} \left( 4 \eta^{-1} R_0^* \right) - \text{Shi} \left( 2 \eta^{-1} R_0^* \right) \right) \left( 1 - 2 \text{ch} \left( 2 \eta^{-1} R_0^* \right) - \right. \]
\[ \left. - \text{ch} \left( 4 \eta^{-1} R_0^* \right) + \text{ch} \left( 4 \eta^{-1} R_0^* \right) \text{Shi} \left( 4 \eta^{-1} R_0^* \right) \right], \tag{6} \]

where \( C \) – the Euler constant.

Minimization of the parameter \( \eta \) leads to a rather cumbersome transcendental equation for finding extreme values \( \eta_{\text{exp}} \), that is not shown in this work.

In figure 1, the relation between the first and the second ionization potentials of a two-electron impurity center with zero nuclear charge in semiconductor QDs in units of Bohr energy \( E_d \), obtained by numerical calculations (curves 1,2,3) is shown.

![Figure 1. Relation between the first and the second ionization potentials of a two-electron impurity center with zero nuclear charge in semiconductor QDs (curves 1, 2, 3), for various values of the QD radius (in Bohr units) \( R_0^* \): 1 – \( R_0^* = 3 \); 2 – \( R_0^* = 1 \); 3 – \( R_0^* = 0.5 \) and in the semiconductor bulk \([1]\) (curves 4, 5, 6) for core \( Z \) of a two-electron impurity center: 4 – \( Z = 0 \); 5 – \( Z = 1 \); 6 – \( Z = 2 \).](image)

As shown in figure 1, the energy of mutual attraction is not compensated by the corresponding Coulomb attraction to the nucleus \((Z = 0)\) because the threshold value of \( E_2/E_d \), from which the existence of a two-electron bound state is possible, is very large. In case of QDs (curves 1, 2, 3 in figure 1), dimensional quantization energy growth and reduction in the QD radius causes reduction in the threshold value of \( E_2/E_d \).

3. The light absorption coefficient at the double photoionization of a two-electron impurity center in a quasi-zero dimensional structure

The atoms of helium and helium-like ions in the ground state are the simple systems, in which it is possible to observe the double photoionization by a single photon. In the study of semiconductor nanostructures, such a reaction is of a particular interest due to a new situation caused by size quantization. In this section, we will look at the photoionization of a two-electron impurity center in the ground state in a semiconductor QD with the wave function of the form:
The wave function of the final state is determined by the product of one-electron wave functions in a spherical QD:

\[ \Psi(\rho_1, \rho_2) = \frac{2^2 \eta^{-2}}{(\text{th}(R_0^{-1} - \rho_1 \eta^{-1}) - \text{cosec}(R_0^{-1}))^2} \rho_1 \rho_2 \eta^{-2} (R_0^{-1}) \].

(7)

The wave function of the final state is determined by the product of one-electron wave functions in a spherical QD:

\[ \Phi(\rho_1, \rho_2) = \Psi_{n,l,m}(\rho_1, \varphi_1, \theta_1) \Psi_{n,l,m}(\rho_2, \varphi_2, \theta_2) \],

(8)

where:

\[ \Psi_{n,l,m}(\rho, \varphi, \theta) = \frac{\sqrt{2}}{R_0 \sqrt{\rho_1}} J_{l+\frac{1}{2}}(k_0 \rho_1) \frac{J_{l+\frac{1}{2}}(\xi_n)}{J_{l+\frac{1}{2}}(\xi_n)} Y_{l,m}(\varphi, \theta) \],

(9)

here \( i = 1, 2 \); \( Y_{l,m} \) – normalized spherical functions; \( l, m \) – orbital and magnetic quantum numbers; \( J_{l}(x) \) – the Bessel functions of the first kind of order \( l \); \( k_0 = \xi_n / R_0 \); \( \xi_n \) – \( n \)-th root of the Bessel function of the \( l \)-th order.

![Figure 2](image_url)

**Figure 2.** The spectral dependence of the absorption coefficient of light in photoionization of two-electron impurity centers in case of \( R_0 = 1 \): 1 – \( E_2 = 0.04 \) eV \( (E_1 = 0.012 \) eV); 2 – \( E_2 = 0.05 \) eV \( (E_1 = 0.015 \) eV); 3 – \( E_2 = 0.08 \) eV \( (E_1 = 0.027 \) eV); \( X = h \omega / E_d \).

The energy of one-electron states undisturbed by impurities in a spherical QD is defined as:

\[ E_{n,l} = \frac{\hbar^2 \xi_n^2}{2m R_0^2} \].

(10)

The effective Hamiltonian of the interaction with the field of the light wave with a single
polarization vector \( \mathbf{e}_\lambda \) and wave vector \( \mathbf{q} \) is determined by the equation:

\[
H_{\text{int}} = -i \lambda_0 \hbar \left( \frac{2m^2 \alpha'}{\varepsilon_0 m \varepsilon^2} I_0 \right)^{1/2} \exp(i\mathbf{qr}) (\mathbf{e}_\lambda \nabla_r),
\]

(11)

where \( \lambda_0 \) – the local field coefficient that takes into account the difference in amplitudes of the local and average macroscopic fields; \( I_0 \) – the light intensity; \( \omega \) – the frequency of absorbed light; \( \varepsilon \) – the static permittivity of the QD material; \( \alpha' \) – the fine structure constant based on the dialectical constant.

The matrix element which determines the amount of oscillator strength of dipole optical transitions of electrons from the ground state of the two-electron impurity center (6) in the state \( \Psi_{n,m,l} (\rho, \varphi, \theta) \) of discrete spectrum of a QD, can be written as:

\[
M = i \lambda_0 \sqrt{\frac{2\pi \alpha'}{\omega}} I_0 \left[ (E_{n,m,l} - E_i) \langle \Psi^*_{n,m,l} (\rho, \varphi_i) \psi^* (\rho_i) \mid \psi (\rho_i) \rangle \right] + \left( E_{n,m,l} - E_i \right) \langle \Psi^*_{n,m,l} (\rho, \varphi_i) \psi^* (\rho_i) \mid \psi (\rho_i) \rangle \right].
\]

(12)

We assume that the variance \( u \) of the QD size occurs during the decay phase of the supersaturated solid solution and is satisfactorily described by the Lifshitz-Slezov equation [5]:

\[
P(u) = \begin{cases} 
3^3 e u^2 \exp \left[ -1 / (1 - 2u / 3) \right], & u < \frac{3}{2}, \\
\frac{1}{2} \left( u + 3 \right)^{7/2} \left( 3 / 2 - u \right)^{11/2}, & u > \frac{3}{2}, 
\end{cases}
\]

(13)

where \( u = \bar{R} / \bar{R}_0 \), \( \bar{R} \) and \( \bar{R}_0 \) – the QD radius and its average value, respectively ; \( e \) – the base of the natural logarithm.

Taking into account the QD size dispersion, the coefficient of impurity light absorption, \( K(\omega) \), can be represented as:

\[
K(X) = \sum_{n=1}^{N} P(u_n) \frac{2^3 \alpha'}{X} \frac{E_i \left( \eta^{-2} + \xi_{\nu} \bar{R}^{-2} \eta^{-2} \right)^{\nu}}{a^2 \bar{R}^{-2} u_n^2 \text{sh}^6 \left( \bar{R} \eta^{-1} \right) \pi \xi_{\nu} \bar{R}^{-4} u_n^{-1} \mid J_{1/2} (\xi_{\nu}) \mid} \times \\
\frac{2^3 \eta^{-3}}{\left( \text{th} \left( \bar{R}_n \eta^{-1} \right) - \bar{R}_n \eta^{-1} \text{cosec} \left( \bar{R}_n \eta^{-1} \right) \right)} \left( 2 \xi_{\nu} \bar{R}^{-2} u_n^{-2} + \left| E_i \right| / E_d + \left| E_i \right| / E_a \right)^2 \\
\times \xi_{\nu}^{-3} \bar{R}^{-3} u_n^{-3} \left[ \xi_{\nu} \bar{R}_n^{-1} + i n^{-1} \left( \xi_{\nu} \bar{R}_n^{-1} - i 2 \eta^{-1} \right) \text{ch} \left( \bar{R}_n \eta^{-1} \right) \right] \\
\times \text{Si} \left( \frac{2}{\sqrt{\pi}} \bar{R}_n \eta^{-3} u_n^{-3} \left( \xi_{\nu} \bar{R}_n^{-1} u_n^{-1} - 3i \eta^{-1} \right) \right) + i \sqrt{\xi_{\nu} \bar{R}^{-1} u_n^{-1} - 3i \eta^{-1} \left( \xi_{\nu} \bar{R}^{-1} u_n^{-1} + i 2 \eta^{-1} \right) \text{sh} \left( \bar{R}_n \eta^{-1} \right) \times \\
\times \text{Si} \left( \frac{2}{\sqrt{\pi}} \bar{R}_n \eta^{-3} u_n^{-3} \left( \xi_{\nu} \bar{R}_n^{-1} u_n^{-1} + 3i \eta^{-1} \right) \right) + i \sqrt{\xi_{\nu} \bar{R}^{-1} u_n^{-1} + 3i \eta^{-1} \left( \xi_{\nu} \bar{R}^{-1} u_n^{-1} - 2i \eta^{-1} \right) \text{sh} \left( \bar{R}_n \eta^{-1} \right) \times \\
\times \text{Si} \left( \frac{2}{\sqrt{\pi}} \bar{R}_n \eta^{-3} u_n^{-3} \right) \\
\end{cases}
\]

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\begin{equation}
\times \text{Ci} \left( \frac{2}{\pi} \mathcal{R} u_n \left( \xi_{a1} \mathcal{R}^{-1} u_n^{-1} - i\eta^{-1} \right) + \sqrt{\xi_{a1} \mathcal{R}^{-1} u_n^{-1} - i\eta^{-1}} \left( \xi_{a1} \mathcal{R}^{-1} u_n^{-1} + i2\eta^{-1} \right) \text{sh} \left( \mathcal{R} u_n \eta^{-1} \right) \right) \\
\times \text{Ci} \left( \frac{2}{\pi} \mathcal{R} u_n \left( \xi_{a1} \mathcal{R}^{-1} u_n^{-1} + i\eta^{-1} \right) \right) \right| \eta^{-1} \left[ \left( \eta^{-2} + \xi_{a1} \mathcal{R}^{-2} u_n^{-1} \right) \mathcal{R} u_n \cos \left( \xi_{a1} \right) - \mathcal{R} u_n \sin \left( \xi_{a1} \right) \right] \times \\
\times \left( \eta^{-2} + 2\xi_{a1} \mathcal{R}^{-2} u_n^{-1} + \xi_{a1} \mathcal{R}^{-2} u_n^{-2} \right) \right) + \left( \eta^{-2} \left( \xi_{a1} \mathcal{R}^{-1} u_n^{-1} - 1 \right) + k_{a1}^2 \left( \xi_{a1} \mathcal{R}^{-1} u_n^{-1} + 1 \right) \right) \text{sh} \left( \mathcal{R} u_n \eta^{-1} \right) \right|^2, \quad (14)
\end{equation}

where \( u_n = \xi_{a1} / \left( \mathcal{R} \left( X - |E_i| / E_d - |E_2| / E_d \right) \right) \); \( N^- \) is an integral part of the solution of the transcendent equation \( \xi_{a1}^2 = 3 \mathcal{R}^2 \left( X - |E_i| / E_d - |E_2| / E_d \right) / 2 \).

The spectral absorption coefficient of the light associated with the double photoionization of two-electron impurity centers is shown in figure 2. As can be seen, the characteristic of double photoionization of helium atoms is the emergence of a “double-hump” profile on the photo-absorption curve, the distance between the peaks in the tops of the spectral curve corresponds to the difference between the ionization potentials. In figure 2, dynamics of the second peak with growth of \( E_2 / E_d \) is also shown: the second peak transforms into a step (curve 2 in figure 2) and then disappears (curve 3 in figure 2). Indeed, with growth of \( E_2 / E_d \) the bond energy of two-electron impurity state grows as well, and at a certain value of \( E_2 / E_d \) the double photoionization becomes impossible.

3. Conclusion

In this work, generalization of the ZRP in case of two-electron impurity centers in QDs was made. In the semi-empirical model of a two-electron impurity center in a spherical QD, the first ionization potential was calculated. It is shown that in contrast to the bulk semiconductor, because of the quantum size effect, the existence of two-electron bound impurity states with zero nuclear charge in QDs is possible only at lower threshold values of \( E_2 / E_d \).

In the dipole approximation in the frame of the effective mass method, the impurity light absorption coefficient for a quasi-zero dimensional structure at the double ionization of a two-electron impurity center by a single photon is calculated. It is shown that a characteristic feature of the spectrum of double photoionization is a “double-humped” profile of the spectral curve. The distance between peaks of the spectral curve is determined by the difference between the first and the second ionization potentials of the two-electron impurity center.

References

[1] Belorusets E D and Grinberg A A On the energy spectrum of multiply charged impurity centers in semiconductors 1978 Solid State Physics 12 1970
[2] Knyr V A and Zaitsev S A The reaction of the double photoionization of atoms in the J-matrix approach (in Russian) 2010 Bulletin of PNU 1(16), 13
[3] Mikhailov A I and Mikhailov I A Double ionization and excitation ionization in the Compton scattering of high-energy photons for metastable states of heliumlike ions 1999 JETP 89 1023.
[4] Krevchik V D and Levashov A V Energy spectrum and optical properties of quantum dot–impurity center complex 2002 Semiconductors 36 208
[5] Lifshitz L M and Sle佐V V Kinetics of diffusive decomposition of supersaturated solid solutions 1958 JETP 8 331