Oscillator strength of quantum transition in multi-shell quantum dots with impurity

V. A. HOLOVATSKY*, I. B. FRANKIV
Chernivtsi National University, Chernivtsi, Ukraine

The theoretical investigation of the oscillator strength of inter-band transition is performed using the variational method and effective mass approximation. The energies and wave functions of the electron and hole ground states are calculated as functions of the position of hydrogen-like donor impurity in multi-shell spherical quantum dots: $ZnS/CdS/SiO_2$ and $CdS/ZnS/CdS/SiO_2$. It is shown that the position of impurity strongly influences on the distribution of probability density of electron and hole location in nanostructure and on the oscillator strength as well. It is proven that the maximal influence of impurity on the intensity of inter-band quantum transitions in multi-shell quantum dots is observed when it is located inside of the potential wells. Electron and hole locations are determined both by the sizes of the wells and position of the impurity. The external charges essentially affect at the intensities of inter-band quantum transition.

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1. Introduction

Modern nanotechnology allows the creation of new devices that use the features of low-dimensional semiconductor systems energy spectra. Recently, complex quantum structures comprising concentric shells of alternating materials surrounding the core, the so-called quantum-dot-quantum-well (QDQW) systems, have been widely investigated. The first achievement in QDQW systems was obtained for CdS particles with HgS shell in 1993 [1]. Afterward, the spherical multilayered barrier-core/well-shell/barrier-shell, and well-core/barrier-shell/well-shell/barrier-shell nanostructures based on CdS, CdSe, ZnS, ZnSe, HgS, and other semiconductor materials were successfully synthesized by modern chemical colloidal methods [2-6] and theoretically investigated [7-12] too. Such semiconductor nanostructures have shown great potential in the fields of biomedical science (fluorescent labels, chemical sensors and biosensors) [13-15], white light-emitted diodes [16-17] and solar cells [18], owing to their novel optoelectronic properties resulting from the size quantization effect, narrow emission and high luminescence efficiency.

The doping of a homogeneous host matrix with acceptor and donor impurities has been traditionally one of the central subjects in semiconductor physics. The presence of charged impurity changes nanocrystals optical properties.

Numerous theoretical works have been published on the bound states of a hydrogen impurity in spherical quantum dots. In the most of them the investigations are related to the impurities (donor or acceptor) which are located in the centre of QD or quantum anti-dot [19-21]. Using the exact solutions of Schrödinger equation, the influence of central impurity on probability density of electron location in the core/shell/well/shell spherical nanosystem has been studied [8]. The calculations were performed for the ground and first excited electron states. It was proven that the impurity essentially affects at the probability density of electron location.

Generally, the impurity can be localized anywhere in QD, even outside of it. Its position influences on the energies and intensities of the quantum transitions. Different approximations for the off-central impurity were used and dependences of the binding energy on the impurity location were obtained in [22, 23].

There is a lack of theoretical research concerning the influence of off-central donor impurity and external charges at the distribution of probability density of electron and hole location in multi-shell QD. The most probable location of quasi-particles in QDs with almost equal sizes of the potential wells is unstable. In this case, even slight influence of the external charge can dramatically change the quasi-particles location in the nanostructure, changing the wave functions overlapping and, in its turn, impacting the intensities of quantum transitions. Such investigations are important for the creation of new types of nanosensors, semiconductor biological labels and improvement of white light sources.

In this paper we present the results of theoretical study for the influence of the off-central impurity on the distribution of probability density of quasi-particle location and oscillator strengths of quantum transitions. The investigation is conducted for the two kinds of QDs: $ZnS/CdS/SiO_2$ (core-barrier/shell-well/matrix-barrier) and $CdS/ZnS/CdS/SiO_2$ (core-well/shell-barrier/shell-well/matrix barrier). The calculations are performed using the variational method together with the effective mass and rectangular potential barriers approximations.

2. Solution of Schrodinger equation for electron and hole in multi-shell quantum dots with off-central impurity

We consider the multi-shell spherical nanostructure composed of the core (0), spherical shells (*i*) and semiconductor matrix (*n*), fig. 1. The impurity is located at r_{imp} distance from the centre of QD. The coordinate system is chosen in such a way: the origin is placed in the centre of the QD and the Oz-axis is passing through the impurity position.

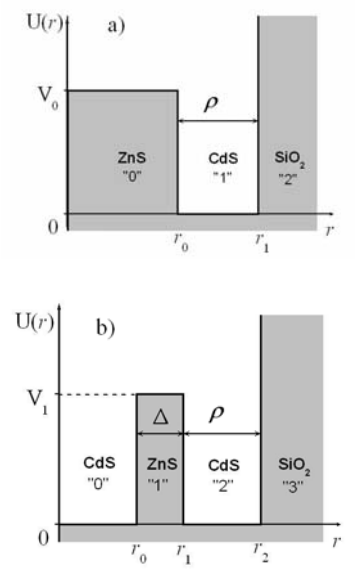


Fig. 1. The scheme of electron potential energy in multi-shell QDs: a) ZnS/CdS/SiO$_2$, b) CdS/ZnS/CdS/SiO$_2$.

The Schrodinger equation for the interacting electron and hole has the form

$$H_e\Psi_{ex}(\vec{r}_e,\vec{r}_h)+H_h\Psi_{ex}(\vec{r}_e,\vec{r}_h)- -\frac{e^2}{\varepsilon\left|\vec{r}_e-\vec{r}_h\right|}\Psi_{ex}(\vec{r}_e,\vec{r}_h)=E\,\Psi_{ex}(\vec{r}_e,\vec{r}_h) \quad (1)$$

In the first approximation for the strong confinement we obtain the equation for electron and hole that interact with the impurity neglecting the electron-hole interaction

$$-\frac{\hbar^2}{2}\vec{\nabla}\frac{1}{\mu(r)}\vec{\nabla}\Psi_{nl}^{e,h}(\vec{r})+[U_{e,h}(r)\mp \mp\frac{e^2}{\varepsilon\left|\vec{r}-\vec{r}_{imp}\right|}]\,\Psi_{nl}^{e,h}(\vec{r})=E_{nl}^{e,h}\,\Psi_{nl}^{e,h}(\vec{r}), \quad (2)$$

where

$$\mu(r)=\begin{cases} m_0^{e,h}, & r\le r_0,\\ m_i^{e,h}, & r_{i-1}<r\le r_i,\\ m_n^{e,h}, & r<r_{n-1}\end{cases} \quad (3)$$

$$U_{e,h}(r)=\begin{cases} V_0^{e,h}, & r\le r_0,\\ V_i^{e,h}, & r_{i-1}<r\le r_i,\\ V_n^{e,h}, & r<r_{n-1}\end{cases} \quad (4)$$

are the electron and hole effective masses and confining potentials, respectively. The sign "-" is taken for the electron and "+" is for the hole.

Generally, the dielectric constant (ε) is the function of quasi-particles and impurity coordinates and QD geometrical parameters, taking into account the particular features of Coulomb interaction in inhomogeneous dielectric medium. Analytically it can be obtained solving the Poisson equation. It is clear that its value smoothly changes between the values of dielectric constants for the semiconductor materials of QD layers (ε_i) and that of the matrix (ε_n). In the case of large difference between the dielectric constants, the polarization charges at the media interfaces, significantly affecting at the potential energy of quasi-particle, should be taken into account. When the differences of dielectric constants of QD shells are not big, ε is chosen as an effective averaged dielectric constant, taking into account the probabilities of quasi-particles locations in QD.

The variational wave functions for the electron and hole ground states are chosen as

$$\Psi_{10}^{e,h}(\vec{r})=A\,\Phi_{10}^{e,h}(r)\exp(\mp\lambda_{e,h}\left|\vec{r}-\vec{r}_{imp}\right|), \quad (5)$$

where A – the normality coefficient, a $\lambda_{e,h}$ – the variational parameter, $\Phi_{10}^{e,h}(r)$ – the wave functions of the ground state for the quasi-particles in QD without impurity. The exponential factor $\exp(\mp\lambda_{e,h}\left|\vec{r}-\vec{r}_{imp}\right|)$ describes the Coulomb interaction between the quasi-particle and impurity.

The electron and hole eigen functions $\Phi_{10}^{e,h}(r)$ are written as

$$\Phi_{10}^{e,h}(r)=\begin{cases} A_0\dfrac{\sinh(\chi_{10}^{e,h}r)}{r}, & r<r_0\\ \dfrac{A_1\sin(k_{10}^{e,h}r)+B_1\cos(k_{10}^{e,h}r)}{r}, & r_0\le r\le r_1\\ A_2\dfrac{\exp(-K_{10}^{e,h}r)}{r}, & r\ge r_1\end{cases} \quad (6)$$

$$\Phi_{10}^{e,h}(r)=\begin{cases} A_0\dfrac{\sin(k_{10}^{e,h}r)}{r}, & r<r_0\\ \dfrac{A_1\exp(\chi_{10}^{e,h}r)+B_1\exp(-\chi_{10}^{e,h}r)}{r}, & r_0\le r\le r_1\\ \dfrac{A_2\sin(k_{10}^{e,h}r)+B_3\cos(k_{10}^{e,h}r)}{r}, & r_1\le r\le r_2\\ A_3\dfrac{\exp(-K_{10}^{e,h}r)}{r}, & r\ge r_2\end{cases} \quad (7)$$

where

$$\chi_{10}^{e,h} = \sqrt{\frac{2m_0^{e,h}(V_0 - E_{10}^{e,h})}{\hbar}}\,,\ k_{10}^{e,h} = \sqrt{\frac{2m_1^{e,h}E_{10}^{e,h}}{\hbar}}\,,$$

$$K_{10}^{e,h} = \sqrt{\frac{2m_2^{e,h}(V_2 - E_{10}^{e,h})}{\hbar}}\,.$$

for *ZnS/CdS/SiO₂* and *CdS/ZnS/CdS/SiO₂* nanostructures, respectively.

The ground state energies for the electron and hole ($E_{10}^{e,h}$) and coefficients (A_i, B_i) are determined by the boundary conditions of continuity for the wave functions and their densities of probability currents [4]. The factor A_0 is defined from the normality condition.

The energies of electron and hole ground states in the QD with impurity are obtained using the condition of functional minimum

$$E_{10}^{e,h} = \min_{\lambda_{e,h}} \iiint \psi_{10}^{e,h^*}(\vec{r}) H_{e,h} \psi_{10}^{e,h}(\vec{r}) d^3\vec{r}\,. \qquad (8)$$

In order to consider the electron-hole interaction, the variational wave function for the exciton is taken as a product of the wave functions of electron and hole interacting with the impurity (5) and the factor describing their Coulomb interaction: $e^{\lambda|\vec{r}_e - \vec{r}_h|}$

$$\Psi_{ex}(\vec{r}_e, \vec{r}_h) = B\,\Psi_{10}^{e}(\vec{r}_e)\Psi_{10}^{h}(\vec{r}_h)\,e^{-\lambda|\vec{r}_e - \vec{r}_h|}\,, \qquad (9)$$

where B – the normality coefficient and λ – the variational parameter.

The variational parameter (λ) and the energy of inter-band transition between electron and hole ground states considering the exciton binding energy are calculated within the minimization of the functional

$$E_{ex} = \min_{\lambda} \iiint \psi_{ex}^{*}(\vec{r}_e, \vec{r}_h) H \psi_{ex}(\vec{r}_e, \vec{r}_h) d\vec{r}_e d\vec{r}_h\,, \qquad (10)$$

where

$$H = H_e + H_h - \frac{e^2}{\varepsilon|\vec{r}_e - \vec{r}_h|}\,. \qquad (11)$$

This minimization is performed using the iteration method.

In dipole approximation, the oscillator strength of quantum transition between electron and hole ground states are proportional to the square of integral of their wave functions overlapping [25]

$$F_{10-10} \sim E^{-1}\left|\int \Psi_{10}^{e}(\vec{r}_e)\Psi_{10}^{h}(\vec{r}_h)\delta(\vec{r}_e - \vec{r}_h)dV\right|^2, \qquad (12)$$

where

$$E = E_{10}^{e} + E_{10}^{h} + E_g - E_{ex}\,. \qquad (13)$$

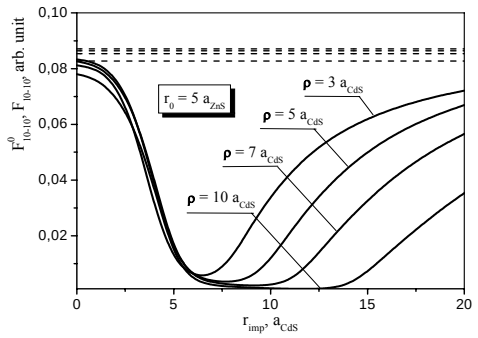
Evidently, the energy of quantum transition is determined by the energies of electron and hole interacting with the impurity and that of electron-hole interaction.

3. Discussion of the results

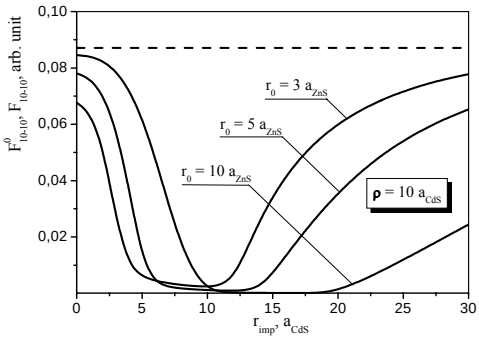
3.1 ZnS/CdS/SiO₂ (core-barrier/shell-well/matrix-barrier)

The numerical calculations are performed using the following physical parameters for ZnS/CdS/SiO₂ nano-structure: $m_0^e = 0{,}28\,m_e$, $m_0^h = 0{,}49\,m_e$, $m_1^e = 0{,}2\,m_e$, $m_1^h = 0{,}7\,m_e$, $m_2^e = 0{,}42\,m_e$, $m_2^h = 1{,}0\,m_e$, $V_0^e = 0{,}5eV$, $V_0^h = 0{,}62eV$, $V_2^e = 2{,}7eV$, $V_2^h = 3{,}9eV$, $\varepsilon_0 = 8{,}25$, $\varepsilon_1 = 5{,}5$, $\varepsilon_2 = 3{,}9$. The oscillator strength of quantum transition between electron and hole ground states as function of donor impurity position in ZnS/CdS/SiO₂ QD is shown in fig.2 (solid curves). The oscillator strength of inter-band transition in the QD without impurity (F_{10-10}^{0}) (dashed lines) is shown for the comparison.

It is clear that the off-centre impurity reduces the intensity of emission. The oscillator strength non-monotonously depends on impurity position for the different sizes of nanostructure composition parts. Such behaviour of functions can be explained analyzing the distribution of probability density of electron and hole location in ZnS/CdS/SiO₂ QD at different positions of impurity, Fig. 3.



(a)



(b)

Fig.2. Oscillator strengths of quantum transition as functions of the impurity position (r_{imp}) in ZnS/CdS/SiO₂ QD: (a) r_0=5a_{ZnS} at ρ=3,5,7,10 a_{CdS}; (b) ρ=10 a_{CdS} at r_0=3,5,10 a_{ZnS}.

Fig. 3 proves that the maximal value of oscillator strength corresponds to the case of central impurity, when it weakly affects at the overlapping of quasi-particles wave functions. The maximal spatial separation of quasi-particles in the nanostructure is observed when the donor impurity is located inside of the potential well. The electron is localized near the impurity and the hole moves from it into the opposite direction. As a result, the overlapping integral reduces and the oscillator strength of inter-band quantum transition approaches its minimum. If the impurity is located at the QD interface or outside of the QD ($r_{imp} \geq r_1$), the electron binding with the impurity diminishes and the oscillator strength increases till the value that corresponds to the QD without impurity.

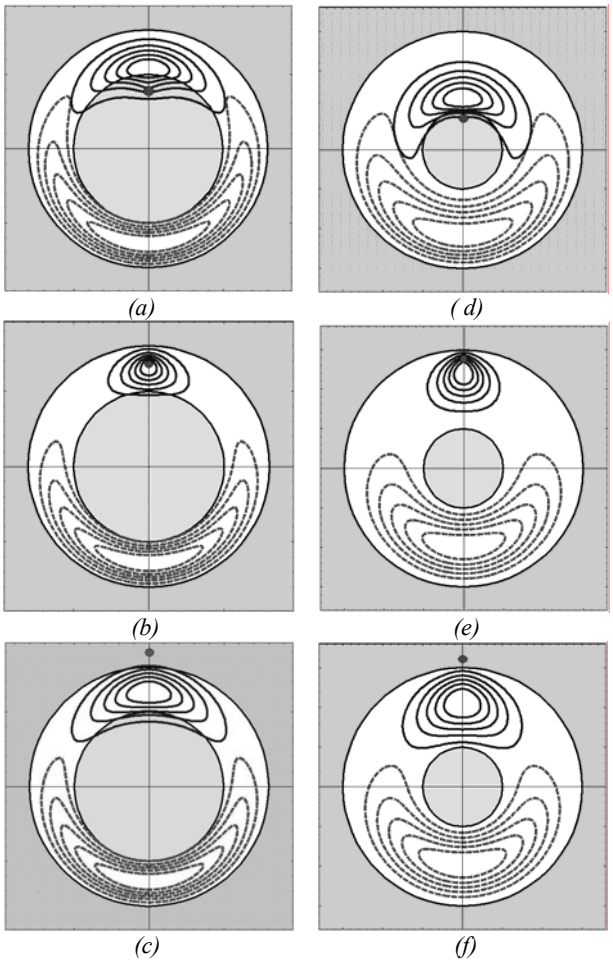


Fig.3. Distribution of probability density of electron and hole location in ZnS/CdS/SiO$_2$ QD with geometrical parameters: r_0=5a_{ZnS}; ρ= 3a_{CdS} (a-c), 10a_{CdS} (d-f) at impurity position: r_{imp} = 4 a_{ZnS} (a, d); r_1 - 1a_{CdS} (b, e); r_1 + 1a_{CdS} (c, f).

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In order to choose the optimal parameters of nanostructure, for which the influence of the external charges would be maximal, in fig.4 the difference between the oscillator strength in QD with impurity at the interface ($r_{imp} = r_1$) and without impurity as function of the barrier-core size at different potential well-shell widths is shown.

Figure proves that the nanostructure with bigger core and shell width is more sensitive to the external chargers. If the core radius increases, all functions saturate and the influence of shell width on the difference of the oscillator strengths become smaller. Thereby, the values: r_0=5$_{ZnS}$ and ρ=15$_{CdS}$ would be the optimal ones.

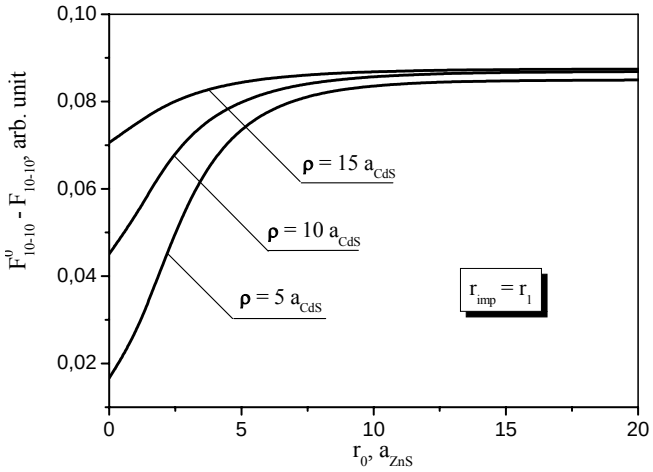

Fig. 4. Dependence of difference between oscillator strengths F^0_{10-10} - F_{10-10} on radius of the core at r_{imp} =r_1 for the different shell widths: ρ=5, 10,15 a_{CdS}.

3.2 CdS/ZnS/CdS/SiO$_2$ (core-well/shell-barrier/shell-well/matrix barrier)

We study CdS/ZnS/CdS/SiO$_2$ QD with almost equal sizes of potential wells formed by CdS core and shell. This nanostructure is characterized by unstable location of quasi-particles in its composition parts. It allows changing the distribution of probability density of electron and hole due to the Coulomb interaction with charged impurity. The computed oscillator strength of quantum transition between electron and hole ground states as function of donor impurity position is shown in fig.5. For the comparison, the calculations are performed for two QDs with the parameters: 1) r_0=10 a_{CdS}; Δ=3 a_{ZnS}, ρ=9 a_{CdS} ; 2) r_0=11 a_{CdS}; Δ=3 a_{ZnS}, ρ=10 a_{CdS}. The both dependences have the similar character. In order to explain them, we are going to analyze the electron and hole distributions of probability densities at different impurity positions, Fig. 6, 7 for system 2).

The non-monotonous character of the oscillator strengths depending on impurity position is caused not only by quasi-particles spatial separation in one of the wells but also by electron tunnelling into the well where the impurity is located and displacing of the hole into the other well.

In Fig. 6, the radial probability densities of electron and hole location in QD with central impurity and without it are shown. One can see that positively charged impurity repulses the hole into external potential well. If the impurity moves to the shell-barrier, the hole-impurity interaction diminishes and the wave functions overlapping increases. If the impurity is located inside of the outer

shell-well it attracts the electron into it, while the hole stays in the core. It is accompanied by dramatic decay of oscillator strength because the overlapping of the wave functions tends to zero. The Coulomb attraction decreases and the electron returns into the core when the external charge is located at the distance more than 1 nm from the centre only. This process is accompanied by dramatic increases of oscillator strength of quantum transition.

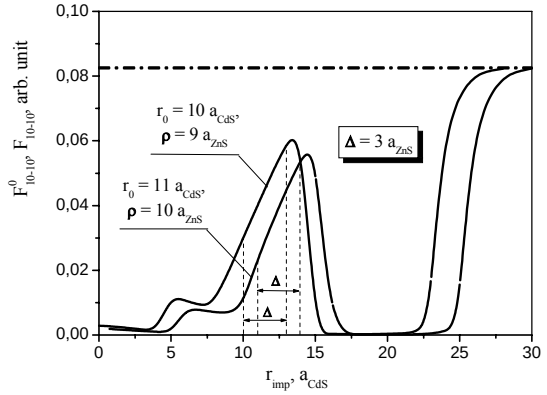

Fig. 5. Oscillator strengths of quantum transition (F^0_{10-10} and F_{10-10}) as functions of the impurity position (r_{imp}) in CdS/ZnS/CdS/SiO_2 QD.

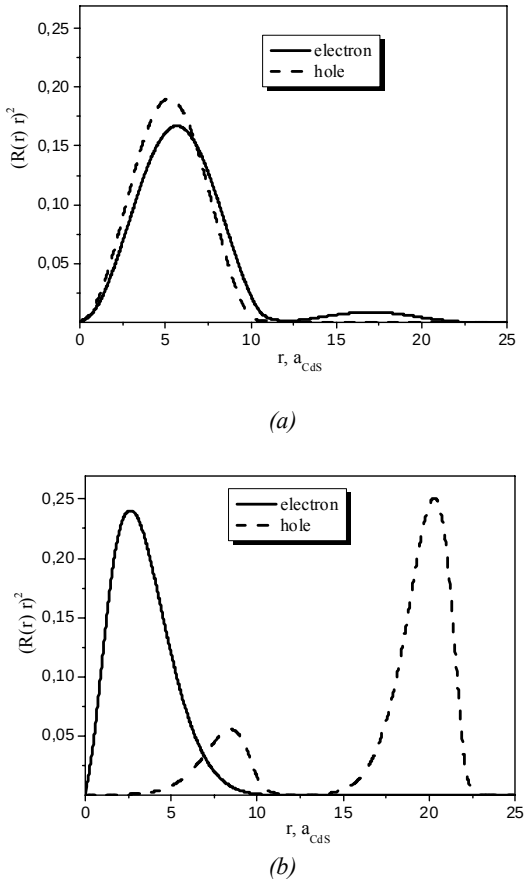

Fig. 6. Distribution of radial probability density of electron and hole location in CdS/ZnS/CdS/SiO_2 nanostructure (a) without impurity, (b) with central impurity

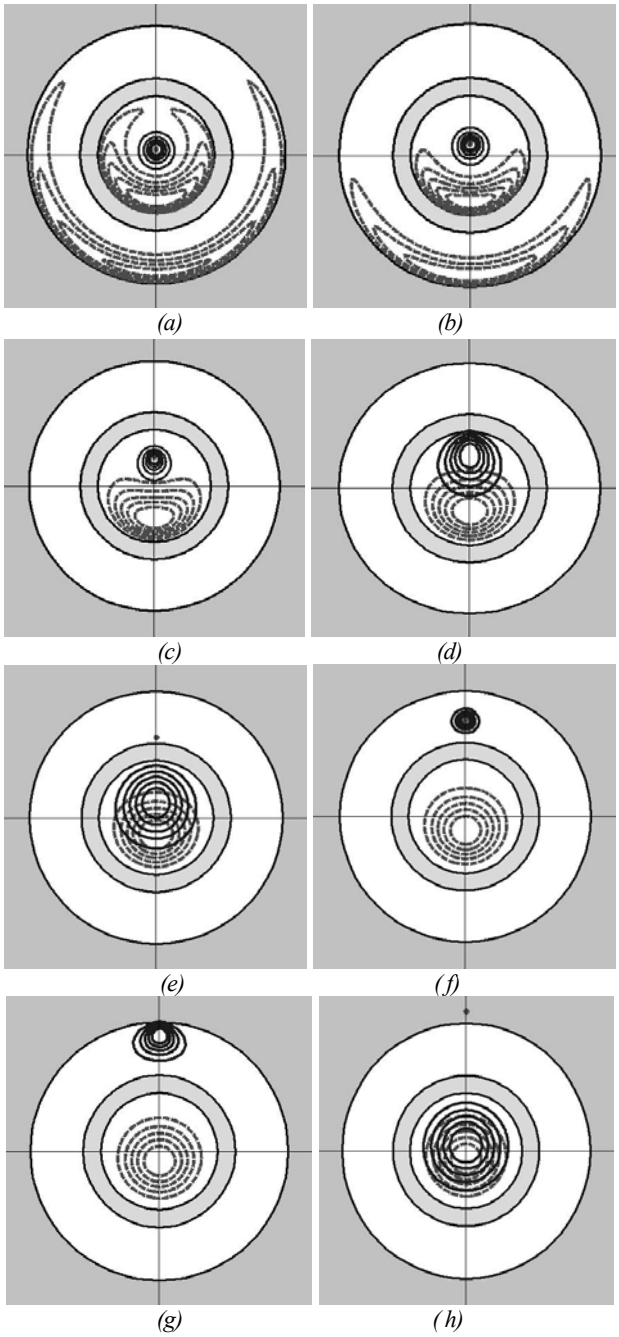

Fig .7. Distribution of probability density of electron and hole location in CdS/ZnS/CdS/SiO_2 QD for different positions of impurity r_{imp}: (a) 1 a_{CdS}; (b) 2 a_{CdS}; (c) 5 a_{CdS}; (d) r_0 ; (e) r_1+1a_{CdS}; (f) r_1+4 a_{CdS}; (g) r_2; (h) r_2+2 a_{ZnS}.

4. Conclusions

The influence of donor impurity and external charges on the probability densities of electron and hole location in the multi-shell quantum dots is theoretically studied using the variational method and the effective mass approximation. The numerical calculations are performed for ZnS/CdS/SiO_2 and CdS/ZnS/CdS/SiO_2 spherical QDs. It is established that the oscillator strength of inter-band quantum transition strongly depends on the position of

donor impurity due to the spatial separation of electron and hole. The tunnelling of quasi-particles into different wells due to their interaction with donor impurity, takes place in CdS/ZnS/CdS/SiO_2 nanostructure with two almost equal potential wells.

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*Corresponding author: ktf@chnu.edu.ua