Book Chapter

The Confinement Effect in Spherical Inhomogeneous Quantum Dots and Stability of Excitons

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Abstract

We investigate in this work the quantum confinement effect of exciton in spherical inhomogeneous quantum dots IQDs. The spherical core is enveloped by two shells. The inner shell is a semiconductor characterized by a small band-gap. The core and the outer shell are the same semiconductor characterized by a large band-gap. So there is a significant gap-offset creating a deep potential well where the excitons are localized and strongly confined. We have adopted the Ritz variational method to calculate numerically the excitonic ground state energy and its binding energy in the strong, moderate and low confinement regimes. The results show that the Ritz variational method is in good agreement with the perturbation method in strong confinement. There is a double confinement effect and dual control. The calculation checks the effective Rydberg R^* at the asymptotic limit of bulk semiconductor when the thickness takes very large values. The excitonic binding energy increases, Thus giving the excitons a high stability even at ambient temperature. These nanosystems are promising in several applications: lighting, detection, biological labeling and quantum computing.

I. INTRODUCTION

The inhomogeneous quantum dots IQDs Core/shell/shell were developed to improve the photoluminescence quantum efficiency QE of single QDs. They have high QE^{1,2} and high photo-stability at room temperature compared to the other nanostructures of low dimensionality. They are highly monodisperses. The earliest inhomogeneous quantum dots were synthesized in 1993 with A. Eychmüller et al.³ The surface to volume ratio is important and there is a high population of atoms on the surface. The shells eliminate effectively the non-radiative centers at the interfaces.^{4,5} The spherical IQDs can be used in colloidal solution or plated on solid substrate. Their physical properties are significantly better when the well is embedded between a core and shell with a large offset. Indeed the strong confinement limits the electrostatic correlations between the exciton localized in the well⁶ and the environment. The excitonic binding energy IS increases remarkably and the excitons acquire a high stability at ambient temperature. These characteristics improve the properties of IQDs. The QDs and IQDs functionalized have shown great potential applications in various fields, such as detection,^{7,8} biolabels,^{7,9} light emitters diodes,^{10,11} in medicine¹² and in quantum information.

II. NANOSYSTEM, MODELING AND THEORY

In a previous paper⁶ we have studied the excitonic transitions in our inhomogeneous QDs core/well/shell with the perturbation method in strong confinement. We showed that the nanostructure is a monocolour nanosource which has wide spectral range from NUV to NIR. In this current work we study the effect of confinement on the excitons and the impact on their stability with a different

method and under all confinement regimes. The nanostructure studied is schematically represented in figure 1, the Table I gives the parameters^{13,14} of the nanosystems studied and the gap-offset $\Delta E_g = E_g(\text{core/shell}) - E_g(\text{well})$.

The well is Indium Antimonide, Mercury Sulfide or Gallium Antimonide which characterized by a direct gap, a small band-gap, a large electric permittivity and a large effective Bohr radius a^* . The core and shell are characterized by a large band-gap; so there is a large offset ΔE_g and the nanostructure is modeled with a profile of infinite potential. The association core/well/shell verifies a lattice mismatch lowers than 10% in order to increase the passivation and increase the QE of photoluminescence.^{1,2} For our theoretical analysis, we will apply the isotropic and non-degenerate parabolic approximations under the effective mass approximation. The Hamiltonian of an exciton is given by:

$$H = -\frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 - \frac{e^2}{\varepsilon \cdot r_{eh}} + V^e + V^h \quad (1)$$

The term $-(\hbar^2/2m_i^*)\nabla^2$ is the kinetic energy of electron (hole); $-e^2/\varepsilon \cdot r_{eh}$ is coulombic interaction and $V^i = V^i(\vec{r}_i)$ is the confining potential given by:

$$V^i(r) = \begin{cases} 0 & \text{if } r_1 < r < r_2 \\ \infty & \text{if } r < r_1 \text{ or } r > r_2 \end{cases}$$

Using the factors $\gamma = m_e^*/(m_e^* + m_h^*)$, $\mu^* = m_e^*m_h^*/(m_e^* + m_h^*)$, $r_{eh} = r$ and taking $a^* = \varepsilon\hbar^2/\mu^*e^2$, $R^* = \mu^*e^4/2\varepsilon^2\hbar^2$ the effective Bohr radius and Rydberg respectively as units of length and energy, the Hamiltonian can be writing:

$$H = \left[-\gamma \cdot \nabla_e^2 - (1 - \gamma) \cdot \nabla_h^2 - \frac{2}{r} \right] + V^e + V^h \quad (2)$$

In the coordinates system (r_e, r_h, r) and by explaining the Laplacian operator the Hamiltonian became:

$$H = \gamma \frac{2m_e^*}{\hbar^2} H_0^e + (1 - \gamma) \frac{2m_h^*}{\hbar^2} H_0^h + \gamma H_1^e + (1 - \gamma) H_1^h + H_2 \quad (3)$$

FIG. 1. Schematic representation of nanosystem and spherical potential profile of confinement.

TABLE I. The parameters of semiconductors used in the IQDs at 300K.^{13,14}

Core/well/shell	Eg (well) (eV)	Eg(eV) Core-shell	ΔE_g (eV)	% Lattice mismatch	$\frac{m_e^*}{m_e}$	$\frac{m_h^*}{m_e}$	a^* (nm) well	R^* (meV) well	ε (well)
ZnSe/HgS/ZnSe	0.5	2.69	2,19	3,14	0.036	0.044	30.41	2.0866	11.36
ZnS/HgS/ZnS	0.5	3.61	3,11	7,56	0.036	0.044	30,41	2.0866	11.36
CdS/InSb/CdS	0.17	2.49	2,32	9,9	0.014	0.43	69.30	0.7481	15.70
ZnSe/GaSb/ZnSe	0.68	2.69	2,01	7,02	0.041	0.4	20.25	2.0545	15.69
CdS/GaSb/CdS	0.68	2.49	1.81	4.32	0.041	0.4	20.25	2.0545	15.69

with the following operators:

$$\begin{cases} H_0^i = -\frac{\hbar^2}{2m_i^*} \left[\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} \right] + V^i \\ H_1^i = -\left[\frac{r_i^2 - r_j^2 + r^2}{r_i r} \frac{\partial^2}{\partial r_i \partial r} \right] i, j = e, h \ (i \neq j) \\ H_2 = -\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] - \frac{2}{r} \end{cases} \quad (4)$$

The energy and the envelope wave function of the exciton are determined by solving the Schrödinger equation who cannot be solved analytically, so we will use the Ritz variational method in the strong, moderate and low confinement regimes. We choose the following trial wave function:^{6,15}

$$\Psi(r_e, r_h, r) = \varphi(r_e)\varphi(r_h)\exp(-\alpha r) \quad (5)$$

The exponential term $\exp(-\alpha r)$ take into account the electron-hole correlation, α a variational parameter and $\varphi(r_i)$ ($i = e, h$) is the wave function of free particle electron or hole given by:⁶

$$\varphi(r_i) = \frac{1}{\sqrt{4\pi}} \frac{1}{r_i} \sqrt{\frac{2}{\Delta r}} \sin(k(r_i - r_1)); \Delta r = r_2 - r_1; k = \frac{\pi}{\Delta r} \quad (6)$$

The ground state E_f and the excitonic binding energy E_b^V are obtained by:

$$E_f = \min_{\alpha} \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (7)$$

$$E_b^V = (E_e + E_h) - E_f \quad (8)$$

E_e, E_h defined the energy of the electron-hole *uncorrelated*. The computation of E_f and E_b^V gives:

$$E_b^V = k^2 - E_f = k^2 - \min_{\alpha} \left[k^2 - \alpha^2 + 2(\alpha - 1) \frac{I_2(\alpha)}{I_1(\alpha)} - \frac{I_3(\alpha)}{I_1(\alpha)} \right] \quad (9)$$

The integrals $I_i(\alpha)$ ($i = 1, 2, 3$) are given by the following expressions:

$$\begin{aligned} I_1(\alpha) &= \int_{r_1}^{r_2} dr_e \int_{r_1}^{r_2} dr_h \int_{|r_e - r_h|}^{r_e + r_h} F(r_1, r_e, r_h) r e^{-2\alpha r} dr \\ I_2(\alpha) &= \int_{r_1}^{r_2} dr_e \int_{r_1}^{r_2} dr_h \int_{|r_e - r_h|}^{r_e + r_h} F(r_1, r_e, r_h) e^{-2\alpha r} dr \\ I_3(\alpha) &= \int_{r_1}^{r_2} dr_e \int_{r_1}^{r_2} dr_h \int_{|r_e - r_h|}^{r_e + r_h} \alpha r_h (r_h^2 - r_e^2 - r^2) G(r_1, r_e, r_h) e^{-2\alpha r} dr \\ G(r_1, r_e, r_h) &= \left[k \frac{\cos k(r_e - r_1)}{r_e} - \frac{\sin k(r_e - r_1)}{r_e^2} \right] \times \frac{\sin k(r_e - r_1)}{r_e} \frac{\sin^2 k(r_h - r_1)}{r_h^2} \\ F(r_1, r_e, r_h) &= \frac{\sin^2 k(r_e - r_1)}{r_e} \frac{\sin^2 k(r_h - r_1)}{r_h} \end{aligned} \quad (10)$$

In the expression of the trial wave function, the exponential term $\exp(-\alpha r)$ take into account the electron-hole correlation so when the variational parameter $\alpha \rightarrow 0$ they are uncorrelated, the excitonic binding energy of ground state E_b tends to 0 and the energy of the ground state E_f tends inferiorly to $E_e + E_h$. If $\alpha \rightarrow +\infty$ the excitonic energy ground state is not defined and this situation is physically unacceptable.

III. RESULTS OF CALCULATIONS AND DISCUSSION

For the IQDs with HgS and GaSb we will calculate numerically the excitonic binding energy E_b^V of the ground state in the strong, moderate and low confinement regimes with the following values of core radius $r_1 = 0,033a^*$; $0,165a^*$; $0,5a^*$; $0,8a^*$; $1a^*$; $2a^*$; $5a^*$ and $10a^*$. The Table II gives for HgS the values of excitonic binding energy of ground state calculated by perturbation and variational methods and gives the uncertainties observed $\delta E_b = |E_b^V - E_b^P|$. For calculation in the perturbation method we used the formula (11).

$$E_b^P(\text{eV}) = 2,88 \frac{1}{\varepsilon \Delta r (nm)} I(m) \quad \text{with} \quad I(m) = \int_0^\pi \frac{\sin^2 x}{x + m\pi} dx \quad (11)$$

For $r_1 = 0.8a^*$ and $m = 1$ the calculation of excitonic binding energy of ground state gives $E_b^V = 12.73R^*$ associated at the variational parameter $\alpha = 0.42$ and with the wave function:

$$\Psi(r_e, r_h, r) = \frac{1}{2\pi} \frac{1}{\Delta r} \frac{\sin(k(r_e - r_1))}{r_e} \frac{\sin(k(r_h - r_1))}{r_h} \exp(-0.42r) \quad (12)$$

The full curves in the figures 2 and 3 represent the energy E_b versus the parameter $m = r_1/\Delta r$ and the dashed curves represent the energy E_b^P calculated with the perturbation method. The figure 2 shows that the binding energy varies with the core radius r_1 and the well thickness Δr ; therefore there is a dual opto-electronic control and a double effect of confinement. When r_1 or Δr decreases the exciton feels the space narrowing along the radial direction and along the circumference. The figure 2 shows

TABLE II. For HgS, the excitonic binding energy values E_b^V and E_b^P calculated by perturbation and variational methods and the uncertainties δE_b for $r_1 = 0.033$; 0.165 ; 0.5 ; 0.8 (a^*).

$r_1(a^*)$	$r_1 = 0.033$			$r_1 = 0.165$			$r_1 = 0.5$			$r_1 = 0.8$		
m	E_b^V	E_b^P	δE_b	E_b^V	E_b^P	δE_b	E_b^V	E_b^P	δE_b	E_b^V	E_b^P	δE_b
0,005	10,70	11,34	0,64	8,60	10,50	1,90	7,00	9,00	2,00	5,40	8,00	2,60
0,01	11,40	11,99	0,59	9,10	10,90	1,80	7,20	9,20	2,00	5,80	8,30	2,50
0,05	15,70	16,30	0,60	12,30	13,70	1,40	9,20	10,50	1,30	7,80	9,30	1,50
0,1	21,01	21,66	0,65	15,30	16,10	0,80	10,70	11,80	1,10	9,20	10,20	1,00
0,2	28,40	29,00	0,60	18,30	19,05	0,75	12,60	13,60	1,00	10,50	11,38	0,88
0,4	37,73	38,33	0,60	22,30	23,00	0,70	14,90	15,78	0,88	11,80	12,63	0,83
0,5	41,05	41,68	0,63	23,80	24,49	0,69	15,60	16,50	0,90	12,15	12,95	0,80
0,6	43,68	44,28	0,60	24,80	25,50	0,70	16,00	16,89	0,89	12,30	13,09	0,79
0,8	47,81	48,38	0,57	26,30	26,95	0,65	16,50	17,31	0,81	12,47	13,26	0,79
1	50,20	50,80	0,60	27,30	27,90	0,60	16,74	17,53	0,79	12,73	13,51	0,78
2	53,30	53,91	0,61	29,60	30,00	0,40	18,25	18,71	0,46	14,10	14,19	0,09

FIG. 2. For HgS (a) and GaSb (b), Binding energy versus m for $r_1 = 0,033; 0,165; 0,5; 0,8(a^*)$.

FIG. 3. (a) Binding energy versus m for $r_1 = 1;2;5;10(a^*)$ and (b) a large scale of the part near 0.

that the binding energy of exciton 1S increases if m increases and this is more pronounced when r_1 is small. This result is confirmed by the variational method⁶ and by Ferrari et al.¹⁶ The variation of excitonic binding energy is different before or after the value $m = 1$, indeed it is stronger if $\Delta r \geq r_1$ and lower elsewhere. The exciton binding energy increases despite the screening effect assured by the high value of the dielectric permittivity (Table I) which reduces the electrostatic interactions and the stability of excitons. The strong confinement provided by the barrier masks and predominates this screening effect. This stability at room temperature gives to the nanostructure a flexibility in use and applications.^{1,8,17}

In figure 2 the full curves correspondent to Ritz variational method and the dashed curves obtained by perturbation method⁶ are in good agreement and the confinement is strong. However there is a slight difference when m is small and when r_1 increases ($r_1 = 0.8a^*$), because in this case the confinement is not strong but intermediate and the perturbation method is invalid. For the value $r_1 \leq 0.5a^*$ the binding energy exceeds 25meV the energy of room temperature and reaches very large values 112.5meV for HgS and 79.09 meV for GaSb. The exciton in bulk HgS or GaSb was barely stable at 25 K with an energy equal 2,1 meV.⁶ In our nanostructure, the exciton in HgS or GaSb becomes very stable at room temperature. This stability increases when Δr decreases, all the more so that r_1 is small. In figure 3, we note that the continuous curves move way when r_1 increases and this is more pronounced with $r_1 = 10a^*$. The perturbation method⁶ is inappropriate in this situation ($r_1, \Delta r < a^*$) because the confinement is stronger. Inflection point appear, the curves change the concavity, approximately for $m = 0.2$.

When m tends to 0, all continuous curves tend towards the same limit $1R^*$ equal to the effective Rydberg. The Ritz variational method allows finding the limit of bulk SC. Indeed, when the well thickness becomes large the material will be equivalent to a bulk semiconductor.

IV. CONCLUSION

In summary we remark a double effect confinement in the spherical IQDs. The strong confinement provided by the infinite barrier gives an important stability to the excitons at ambient temperature, which gives the IQDs great flexibility in use and applications. The binding energy of exciton on the ground state 1S increases when Δr decreases, more pronounced for r_1 smaller. This property promotes the radiative recombinations and increases the luminescence for the IQDs. We showed that in strong confinement the perturbation method and the Ritz variational method are in good agreement; but in the low confinement regime the perturbation method is inappropriate. When the parameter m tends to 0, all continuous curves of the excitonic binding energy of ground state tend approximately towards the same limit equal to the effective Rydberg value $1R^*$ which defines the bulk semiconductor. The previous excitonic properties in IQDs could open up to new avenues of research in SC physics.

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