Stokes Shift in Quantum Dots: Origin of Dark Exciton

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Abstract— **A very interesting feature of semiconductor quantum dots(QDs) is the redshift of emission peaks with respect to absorption spectra and its size dependence. The red shift of the emission spectra with respect to absorption spectra is known as Stokes shift, which is commonly observed in semiconductor quantum dots(QDs) and is one of the most important quantities that determine the optical properties of QDs. As the radius increases the redshift decreases and disappears beyond a certain radius. The mechanism of Stokes shift in semiconductor quantum dots is investigated by calculating the energy of the excitonic states. We have taken into account all possible contributions to the total electronic energy in the dot, i.e, dielectric mismatch between dot and surrounding medium, the effects of finite barrier height and electron-hole exchange interaction. The Stokes shift is calculated as a function of radius of dot and compared with experimental data on two different semiconductor based quantum dots. These results provide evidence for exchange splitting of excitonic states, as the mechanism of Stokes shift in QD.**

I. INTRODUCTION

The red shift of the emission spectra with respect to absorption spectra is known as Stokes shift, which is commonly observed in semiconductor quantum dots(QDs) and is one of the most important quantities that determine the optical properties of QDs. Several observations of Stokes shift and related phenomena of long spin relaxation times in QDs[1-5]and several investigations of their underlying mechanisms[6-11]have been reported in the literature. However the underlying mechanism of Stokes shift is still far from clear. In case of semiconductor QDs, this shift decreases with the increase in radius of the dot and disappears beyond a certain radius. The red shift, principally, occurs if either the top of the valence band is an optically passive state (say P state) or if the electron and the hole are in a triplet state. Absorption of a photon from the top of the valence band in such cases is not allowed and is possible only from an optically active state lying deeper in the valence band. The exciton, once formed after absorption, can not decay to the top of the valence band by direct dipole transition and hence is called ``dark exciton''[1]. Deexcitation eventually takes place with the help of phonons thus giving rise to red shifted photons.

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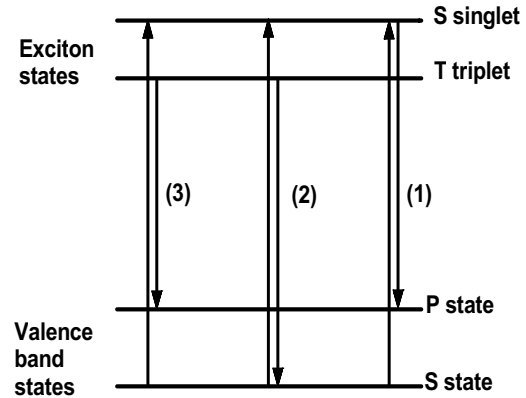
Fig. 1. The schematic representation of excitation-deexcitation processes taking place at the band edges.

Two different mechanisms[2,9]have been proposed to explain the origin of Stokes shift in semiconductor QDs, as shown in Fig. 1. Absorption takes place from the S-state which lies deeper than the P-state in the valence band to form an exciton in the singlet state of the electron and hole. According to the first mechanism, (1) of Fig. 1. deexcitation takes place into the P state with the help of phonons giving rise to a Stokes shift by an amount ΔE_{SP} representing the difference in energy between the exciton states formed with S and P hole states[9]. According to the second mechanism the exciton in the singlet state first thermalizes into a triplet state from where it deexcites with the help of phonons either (a) to the deeper lying original S state, (2) of Fig. 1, giving rise to a Stokes shift by an amount ΔE_{ST} representing the singlet triplet splitting(Ref. 2), or (b) to the P state at the top of the valence band, (3) of Fig. 1, with the Stokes shift given by $\Delta E_{SP} + \Delta E_{ST}$.

We investigate the origin of Stokes shift in III-V(InAs) and II-VI(CdSe) semiconductor based QDs by calculating the energies of excitonic states. We have taken into account the dielectric mismatch effects, the effect of finite barrier height and the effect of the electron hole exchange interaction and then compared the results with experimental data. InAs and CdSe are chosen because of their (i) different crystal structures, (ii) different crystal field effects which is zero in zinc blende structures(i.e InAs) but significantly large in wurtzite structure(CdSe), (iii) different effective masses which is small in InAs, but large for CdSe and (iv) different nature of bonds. It has been observed experimentally[1,2,4] that the red shift decreases with radius and disappears beyond a certain radius. Essentially, the strong

dependence of Stokes shift on the radius of the QD, is used to investigate the origin
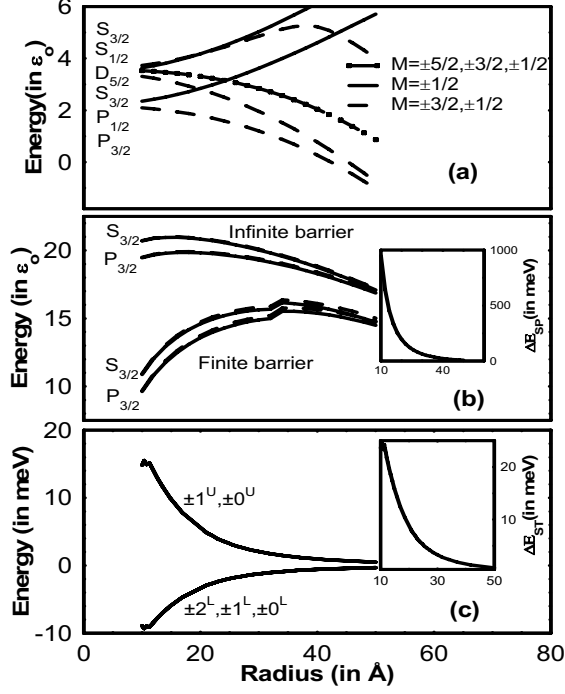

Fig. 2. The energy levels in units of $\mathcal{E}_o$ for zinc blende InAs QDs as a function of R in the (a) absence and (b) presence of e-h Coulomb interaction(without exchange). Eigenvalues in the absence (ε=1) as well as presence(ε=5) of dielectric mismatch effects are also shown in (b) for both the cases of infinite and finite barrier. (c) eigenvalues including e-h Coulomb and exchange interactions. The states are labelled with F_z with superscripts standing for upper and lower state.

of Stokes shift in QDs based on these semiconductors(InAs, CdSe).

II. CALCULATION DETAILS

Optical transitions from the electron state $\Psi_e(r) = j_0\left(\dfrac{\alpha_1^0}{R}r\right)Y_{00}(\theta,\phi)|S\alpha\rangle$, where $|S\alpha\rangle$ are the Bloch functions of the conduction band and α_1^0 is the first zero of $j_0(kr)$, are possible only to hole states in the valence band which have the S-state as a component because $\int Y_{Lm}Y_{00}d\Omega = \delta_{L,0}\delta_{m,0}$. The optical transition probability from the bottom of the conduction band to a hole state in the valence band is given by [12]

$$P_{\alpha\beta} = \left|\int dr\, r^2 j_0\left(\frac{\alpha_1^0}{R}r\right)(cR_0(r))\right|^2 \left|\langle u_\mu\beta|e\hat{p}|S\alpha\rangle\right|^2 \text{ where c is}$$

the component of the S-state $R_0(r)$ in the hole wavefunction, β is the spin projection of the removed electron in the hole state and u_μ are the Bloch wavefunctions of the hole states at the valence band top. $P_{\alpha\beta}$ is zero if $\alpha\neq\beta$. Optical transitions from the bottom of the conduction band to the top of the valence band is not possible if either (1) the hole state does not have a component of the S-state (i.e if c=0), or (2) the spin projections of the removed electron in the hole state and the electron in the conduction band are not equal, $\alpha\neq\beta$. Since the hole spin is obtained by flipping the spin of the
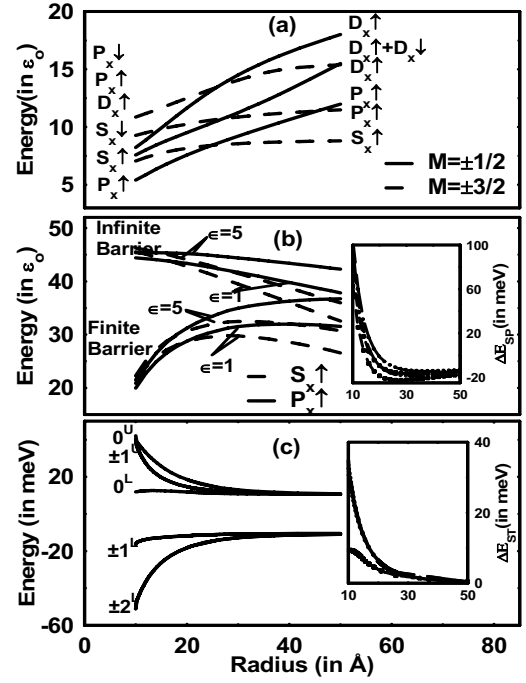

Fig. 3. The energy levels for wurtzite CdSe QDs in the (a) absence and (b) presence of e-h Coulomb interaction and dielectric mismatch effects(without exchange) for both the cases of infinite and finite barrier. The states are labelled as $|S_x\downarrow\rangle$, $|P_x\uparrow\rangle$ etc, where capital letters represent the dominant **L** present and the subscripts stand for X-, Y-like or Z-like states, the arrow indicating the spin state. (c) eigenvalues including the e-h Coulomb and exchange interactions.

removed electron, it follows that optical transitions are not possible if the spins of the electron and the hole are parallel i.e if they are in a triplet state. Thus, if the top of the valence band is a P-state, or the electron and the hole are in a triplet state, a *dark exciton* is formed.

The exciton states are obtained from the Hamiltonian

$$H = H_e + H_h + H_{so} + V_{e-h} + V_{Pol-s} + V_{Pol-eh} \qquad (1)$$

where H_e, H_h, H_{so}, V_{e-h} are the electronic Hamiltonian, the hole Hamiltonian, the spin-orbit interaction and the e-h Coulomb interaction respectively given in Ref.9 and 13. The last two terms represent the surface polarization energies arising due to the difference in the dielectric constants between the semiconductor quantum dot and the surrounding medium[14]. V_{Pol-s} is the self energy of the electron and hole due to their image charges and V_{Pol-eh} is the mutual interaction energy between the electron and hole via image charges. The excitonic states obtained from Eq.1 will be split further due to exchange interaction[2] H_{ex} between the electron and hole.

III. RESULTS AND DISCUSSION

Since the nature of the state at the top of the valence band plays a pivotal role in the formation of dark and bright excitons, we first investigate the hole states for both the zinc-blende and wurtzite structures using the **k.p**
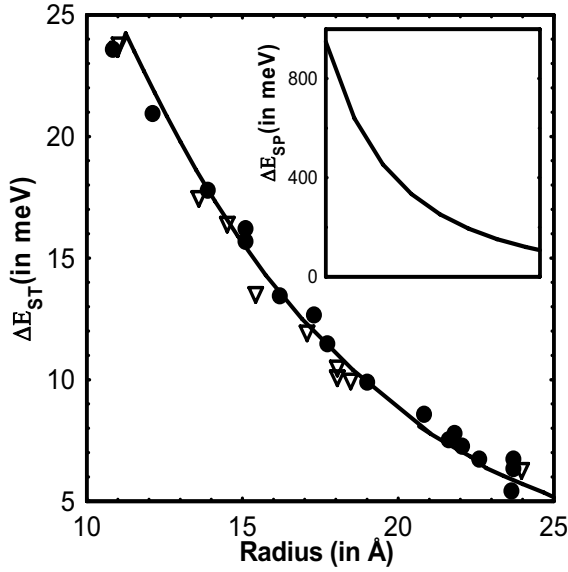
Fig .4. The singlet triplet splitting in InAs for dielectric mismatch ratio ε=5 for the finite barrier case. The curves for no dielectric mismatch case ε=1 superimpose on the curves for ε=5. The inset gives the energy differences of S and P states. Solid circle and empty inverted triangle represent experimental data for InAs QDs, taken from Ref.4.

hole Hamiltonian H_h+H_{so} given in Ref.15. The energy eigenvalues of the hole states without inclusion of excitonic effects as a function of dot radius for InAs(zinc-blende structures) and CdSe(wurtzite structures) are shown in Figs. 2(a) and 3(a) respectively. These eigenvalues get modified when Coulomb interaction between electron in the conduction band and hole in the valence band are taken into account. The corresponding results including excitonic effects are shown in Figs. 2(b) and 3(b) respectively.

From Fig. 2(a) we observe that in InAs the optically passive $P_{\frac{3}{2}}$ is the ground state which lies below the first optically activate $S_{\frac{3}{2}}$ state. The states are labeled $S_{\frac{3}{2}}$, $P_{\frac{3}{2}}$ etc where the capital letters correspond to the lowest **L** present and the subscripts gives the total angular momentum **F'**= **L+I+S**, where **L** is the orbital angular momentum, **I**=1 is angular momentum of the Bloch wavefunction at the valence band top and **S** is the spin of the hole. The difference in energy between the optically passive $P_{\frac{3}{2}}$ state and the optically active $S_{\frac{3}{2}}$ state decreases as the radius of the dot increases and eventually $S_{\frac{3}{2}}$ becomes the ground state at around R ~ 50Å. Hence dark exciton formation and associated Stokes shift will be observed below this radius.

For the wurtzite structure, the Hamiltonian is axially symmetric and only the z-component $M=L_z+I_z+S_z$ of the total angular momentum is conserved. In Fig.3(a) the energies are plotted in units of $\varepsilon_o = \frac{\gamma_1}{2m_o}\left(\frac{\hbar}{R}\right)^2$ (γ_1 is a Luttinger parameter). The energy of the S state decreases as $\frac{1}{R^2}$ but in units of ε_o is independent of R and hence
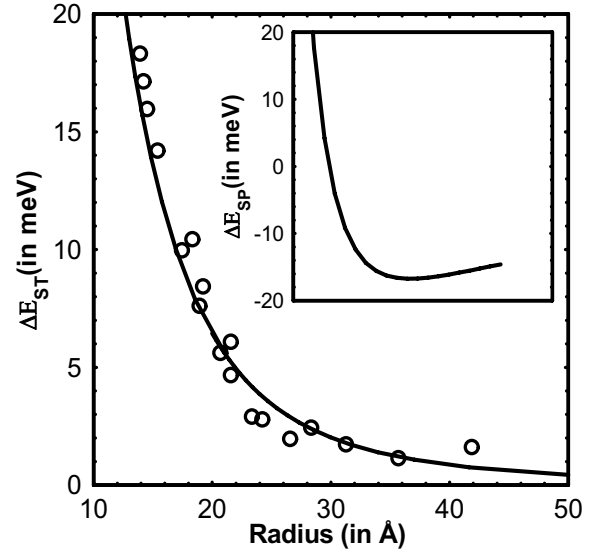

Fig. 5. The singlet triplet splitting in CdSe for dielectric mismatch ratio ε=5 for infinite barrier case. The inset gives respectively for ε=3. Empty circles represent experimental data for CdSE QD, taken from Ref.2.

the state is relatively flat. It is observed that for CdSe the optically active S state $\left|S_x \uparrow\right\rangle$ is not the ground state at R~10Å but the optically passive state $\left|P_x \uparrow\right\rangle$ with $M=\frac{1}{2}$ lies below the S state. The energy of $\left|P_x \uparrow\right\rangle$ in units of ε_o has an upward slope as a function of radius and crosses the relatively flat $\left|S_x \uparrow\right\rangle$ state with $M=\frac{3}{2}$ at R~28Å. Dark exciton formation and Stokes shift is predicted for CdSe below R~28Å.

When the Coulomb interaction between the electron in $1S_e$ state and the hole is taken into account, the energies decrease. The decrease in energy of S-state is more than that of P state, the overlap between $1S_e$ state and S state of the hole being greater. This causes the crossing between S and P states to occur at lower values of R as can be seen from comparison of Figs. 2(b) and 3(b) with the corresponding Figs. 2(a) and 3(a). The differences between the excitonic S and P states ΔE_{SP} as a function of R, are shown in the insets to Figs. 4 and 5.

The surface polarization charges arising due to the dielectric mismatch between the dot and the surroundings also affect the excitonic energies. The contributions of self energy V_{Pol-s} and attractive energy V_{Pol-eh} are opposite in sign and comparable in magnitude[16]. Hence the dielectric mismatch effects are greatly reduced with the net effect being an increase in energy depending on the amount of dielectric mismatch between the dot and the surrounding. The increase in energy for the P state is more than that for the S state resulting in a crossover to occur at a lower dot radius. This can be seen from Figs.2(b) and 3(b) which gives the comparison between zero and finite dielectric mismatch, i.e ε=1 and ε=5 where $\varepsilon = \frac{\varepsilon_{dot}}{\varepsilon_{surrounding}}$. The self energy of a charge confined to a spherical dielectric is minimum[17]at r=0. Since $\left\langle r^2 \right\rangle$ for the P-state is larger compared to that for

the S-state, the self energy V_{Pol-s} is higher for the P-state. But the attractive energy V_{Pol-eh} is higher for the S state compared to the P state. This leads to a higher net increase of polarization contribution $[V_{Pol-s} + V_{Pol-eh}]$ for the P-state as compared to the S-state and hence to a shifting of the S-P crossover to lower values of R as can be seen from Figs. 2(b)and 3(b).

Another cause of dark exciton formation and the consequent Stokes shift is the splitting of the active exciton states due to electron hole exchange interaction[2] $H_{ex} = \left(-\dfrac{2}{3}\right)\varepsilon_{ex}(a_o)^3\delta(\vec{r}_e - \vec{r}_h)\sigma.J$ where ε_{ex} is the exchange strength constant, a_o the lattice constant, σ the Pauli spin matrices representing the electron spin and J is the hole spin matrix. The exchange interaction gives rise to a splitting between triplet and singlet state of the electron and hole, with the triplet state lying lower in energy. The triplet state being passive, excitation takes place to the higher singlet state. Deexcitation can take place from the triplet state reached by thermalization, thus giving rise to a red shift of the emmision spectra with respect to the absorption spectra.

In InAs the first optically active S state (Fig. 2(a)) has total angular momentum $F'=\dfrac{3}{2}$ ($L=0,I=1,S=\dfrac{1}{2}$) and is fourfold degenerate. The $1S_e$ electron state in the conduction band being doubly degenerate, the exciton states are eightfold degenerate in the absence of exchange interaction. The exchange interaction splits these degenerate levels into two: the lower optically passive triplet state with $F=2(F=F'+S_e)$ and the upper optically active singlet state with $F=1$ (Fig. 2(c)). The difference in energies ΔE_{ST} between the singlet and triplet states as a function of dot radius is shown in Fig. 4. ΔE_{ST} decreases with R and vanishes at R~35Å. The exchange interaction is enhanced with decrease in radius because of the increase in the overlap of electron and hole wavefunctions due to confinement.

In CdSe (Fig. 3(c)) the ground state with $F_z=\pm2^L$ can be obtained by coupling a hole with $M = \pm\dfrac{3}{2}$ with electron state with $\left(S_e\right)_Z = \pm\dfrac{1}{2}$. Since these combinations form triplet states, the ground state with $F_z=\pm2$ is optically passive and forms a dark exciton. The first excited state with $Fz=\pm1^L$ can be obtained either by coupling $M = \pm\dfrac{3}{2}$, $\left(S_e\right)_Z = \mp\dfrac{1}{2}$ or alternatively by $M = \pm\dfrac{1}{2}$ with $\left(S_e\right)_Z = \pm\dfrac{1}{2}$. The state $\pm1^L$ will be a mixture of singlet and triplet states and will be optically active. The difference in energies ΔE_{ST} between the optically passive ground state and the first optically active excited state as function of R for CdSe is shown in Fig. 5. As in the case of InAs, ΔE_{ST} for CdSe also decreases with R and vanishes around R~50Å.

As seen from Figs. 2 and 3 curves corresponding to finite barrier case lie lower than infinite barrier case. This is due to the penetration of a substantial amount of electron wavefunction outside the dot giving rise to lower eigenvalue of the electron wavefunction.

Having theoretically calculated ΔE_{SP} and ΔE_{ST} we are in a position to investigate the various mechanisms for Stokes shift given in Fig. 1 by comparison with experimental data. In Figs. 4 and 5 are shown the plots of ΔE_{ST} as a function of the dot radius together with the experimentally observed Stokes shift for CdSe and InAs respectively. ΔE_{SP} as a function of R for these cases are shown in the insets of the corresponding figures. It is observed that ΔE_{SP} is much larger than the experimental red shift for InAs. For CdSe, as seen from the inset of Fig..5 at R~13Å ΔE_{SP} is almost the same as the experimental Stokes shift but for larger values of R the experimental values are much higher. It is seen from Figs. 4 and 5 that ΔE_{ST} fits the experimental data rather well.

IV. CONCLUSIONS

The red shift of the emission spectra with respect to the absorption spectra has been investigated in III-V and II-VI semiconductors based QDs. The excitonic states have been calculated for both the zinc-blende and wurtzite crystal structures by taking into account all possible contributions to the total energy. Our theoretical results have been compared with the experimental data on InAs and CdSe QDs, and based on our analysis we conclude that the Stokes shift observed in QDs is caused by the splitting of the exciton states by the electron hole exchange interaction through the deexcitation mechanism no. 2, as shown in Fig. 1.

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