Effect of Wannier-Mott Exciton on Semiconductor Quantum Dot Photo-Absorption Spectra

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A review of the Wannier-Mott exciton and the quantum dot as a spherical infinite potential well are presented and used to analyze the effect of the exciton binding energy and quantized energy states on absorption spectra for semiconductor nanocrystallites. The ratio of semiconductor to exciton Bohr radius is used to categorize the exciton and confinement influence on absorption spectra into three regimes.

I. Introduction

Quantum dots have become widely discussed and investigated for their size-tunable electrical and optical properties. They exhibit optical and electrical properties intermediate between bulk material and atoms. The quantization of optical transitions due their small size (~10-100Å) give rise to the nickname artificial atoms.[1]

The absorption and emission spectra of a quantum dot are not only affected by its physical size, but also by the dielectric constant of the semiconductor. The effect can be studied by considering the free electron and hole that are created when absorption of a photon occurs. This pair can remain bound through Coulomb attraction forming a quasi-particle known as the exciton.[2] This attraction affects the semiconductor optical and electronic transport properties and is the topic of discussion within this paper.

Many intricacies exist in physical semiconductors, such as phonon interaction during indirect absorption and the complex structure of the valence band in nanocrystals with an infinite potential barrier. This paper shall aim to qualitatively explain the influence of excitons on the optical transitions found experimentally in quantum dots, and thus some of these intricacies will be omitted that are necessary for more quantitative descriptions.[3]

II. Excitons

The separation of valence and conduction energy bands in a semiconductor dictates the necessary energy for photon absorption to occur. In the direct case, the valence maximum and conduction minimum correspond to the same electron momentum state $\boldsymbol{k}$. For the indirect case, the assistance of phonons is required to balance the momentum offset $\Delta\boldsymbol{k}$ in the upper and lower bands. Taking the direct case, the energy threshold for photon absorption is

$$\hbar\omega > \mathrm{E_g} \tag{1}$$

where E_g is the band gap of the bulk semiconductor.[4]

However, this absorption threshold is lowered by the Coulomb potential of the exciton, shown in Figure 1. The spacing between the conduction band minimum and ground exciton energy states is termed the binding energy of the exciton. It is worth noting, the exciton can transport energy throughout the crystal by simple diffusion process without carrying a net charge when the group velocities of the electron and hole are equal.

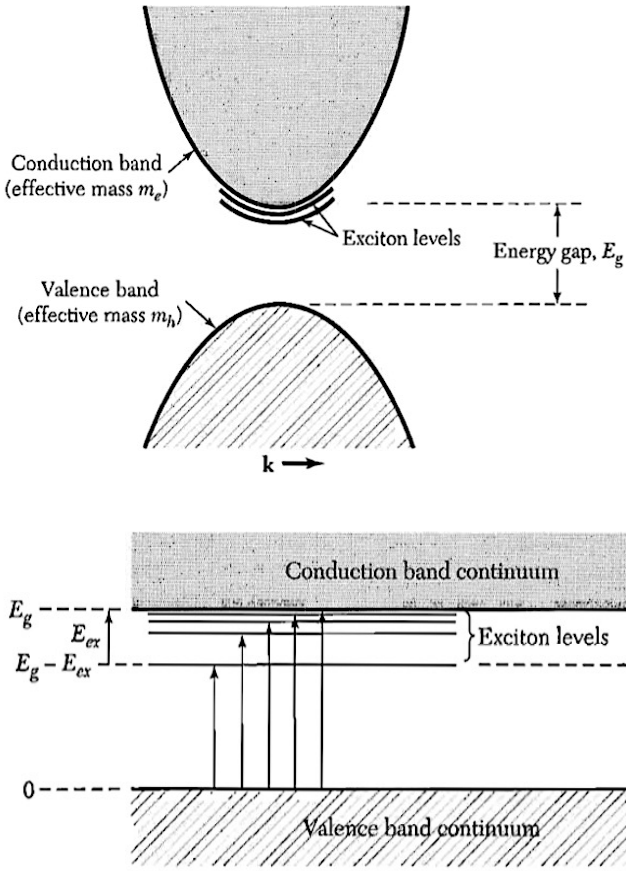

Figure 1. (Top) Exciton energy levels shown on band gap diagram. (Bottom) Energy levels of an exciton created in a direct process where $\boldsymbol{k}$ is neglected for clarity. Optical transitions from the top of the valence band are shown by the arrows.[4]

Two approximations have been established to describe the exciton binding energy. The Wannier-Mott exciton models weakly bound quasi-particles with separation larger than the semiconductor lattice. Conversely, Frenkel excitons correspond to tightly bound excitons with separation on the atomic order.[5] It is accepted that the Wannier-Mott model encompasses excitons found in semiconductors, therefore further discussion of Frenkel excitons is omitted from this text.

Wannier-Mott Exciton. The Wannier-Mott exciton is derived by approximating the exciton as a single isometric electron-hole pair. As these particles are in a periodic potential caused by the semiconductor crystal they have a reduced effective mass given by

$$\mu = \frac{m_e m_h}{m_e + m_h} \tag{2}$$

where m_e (m_h) is the effective electron (hole) mass.[6]

The Coulomb potential generated by the exciton electron-hole pair is given by

$$V(a) = -\frac{e^2}{\kappa a} \tag{3}$$

where κ is the dielectric constant of the semiconductor, e is the charge of an electron and a is the distance of charge separation.

Exciton binding energy levels can be solved for by way of the Schrödinger equation $\left[H\psi_{ex} = E\psi_{ex}\right]$with

$$H = -\frac{\hbar^2}{2\mu}\nabla_{e,h}^2 - V(a) \cdot \tag{4}$$

The Schrödinger equation now takes on the same form as the hydrogen atom whereby a simple modification is completed by replacing the electron-proton atom with the electron-hole exciton and multiplying the Coulomb term by the dielectric strength of the semiconductor κ.

The effect of the binding energy levels is given by

$$E_n = E_g - E_{ex} \tag{5}$$

where n is the quantum number and

$$E_{ex}(n) = \frac{\mu e^4}{2\hbar^2\kappa^2 n^2} \tag{6}$$

are the exciton binding levels. Further simplification for analysis is possible by considering the Bohr radius,

$$\mathrm{a_B} = \frac{\hbar^2\kappa}{\mu e^2} \tag{7}$$

of the exciton. Substituting equations (6) and (7) into equation (5) gives,

$$\mathrm{E_n} = \mathrm{E_g} - \frac{\mathrm{e}^2}{2\kappa \mathrm{n}^2 \mathrm{a_B}} \cdot \tag{8}$$

This result shows discrete energy levels exist less than the band gap and the binding energy is proportional to $\sim 1/a_B$. Thus, the absorption threshold is lowered and equation (1) can be rewritten as

$$\hbar\omega > E_n \, . \tag{9}$$

The ground state (n=1) of the exciton is referred to as the modified Rydberg, resulting in energies on the order of 1meV to 1000eV depending on the dielectric constant κ. Excitons found in semiconductors of interest have binding energies E_{ex} of 14.7meV (CdSe) to 29meV (CdS).

The exciton binding energy and the band gap can be found experimentally from the shape of the absorption curve obtained through optical transition analysis such as photoluminescence (PL) measurements. An example is shown in Figure 2.

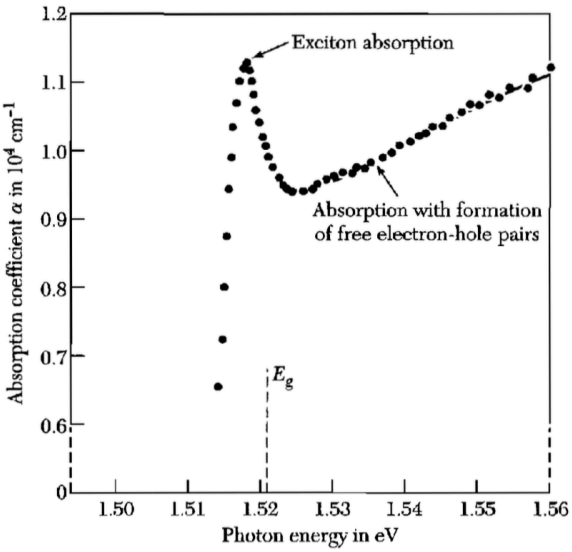

Figure 2. Optical absorption of GaAs at 21K for photons of energy near the band gap. (E_G = 1.521 eV, E_{ex} = 3.4 meV).[4] The photon energies are near infrared with $\lambda_{1.5eV}$ of 826nm and $\lambda_{1.56eV}$ of 795nm.

III. Energy States of Quantum Dot: Spherical 3D Infinite Potential Well

By approximating a quantum dot as a spherical three-dimensional quantum well, the Schrödinger equation can be used to solve for its energy states. The quantized energy state solution of a spherical quantum dot for electrons and holes is given by,

$$E_{n,m}^{e,h} = \frac{\phi_{n,m}^2 \hbar^2}{2m_{e,h}a^2} \tag{10}$$

where $\phi_{n,m}$ is the m^{th} root of the spherical Bessel function of quantum number n (with ground state $\phi_{l,0} = \pi$).[7] This result shows a straightforward dependence of the energy levels on the confinement size. As the size of the dot a is confined, the energy levels increase into the conduction band as $\sim 1/a^2$.

Updating equation (5) we can write the absorption spectra as

$$\hbar\omega = E_g\text{-}E_{ex} + E_{n,m}^e + E_{n,m}^h \tag{11}$$

or by expansion,

$$\boxed{\hbar\omega = \mathrm{E_g} - \frac{\mathrm{e}^2}{2\kappa \mathrm{n}^2 \mathrm{a_B}} + \frac{\phi_{\mathrm{n,m}}^2 \hbar^2}{2\mu \mathrm{a}^2}} \tag{12}$$

IV. Three Confinement Regimes.[7]

The ratio of semiconductor radius a to the exciton Bohr radius a_B governs the optical properties of the nanocrystal. The Coulomb potential changes as $\sim 1/a_B$ whereas the energy state solution changes as $\sim 1/a^2$. We can categorize these ratios into three confinement regimes: $a \gg a_B$ (weak), $a \sim a_B$ (intermediate), and $a < a_B$ (strong).[7]

The ground state absorption spectra can easily be found, taking n=1 *and* $\phi_{1,0} = \pi$ and is given by

$$\hbar\omega = E_g - \frac{e^2}{2\kappa a_B} + \frac{\pi^2\hbar^2}{2\mu a^2}. \qquad (13)$$

The ratio of the second term E_{ex} to the third $E_{n,m}$ term is plotted in Figure 3, taking a_B = .7*nm,* effective masses m_e=.417, m_h=1.477*,* dielectric constant κ =7.9 and a range of quantum dot sizes from .1 to 10*nm* for CuCl.[8]

a. Weak Confinement Regime. The weak confinement regime occurs when the quantum dot radius a is much larger than the exciton Bohr radius a_B. In this case, $E_{n,m}$ is relatively small compared to E_{ex} and the weight of the exciton binding energy is the most influential of the regimes.

Turning to equation (13) and taking $a \gg a_B$, the second term E_{ex} becomes much larger than the third term $E_{1,0}$ due to the larger radius a being squared in the denominator.

If we calculate these terms for CuCl nanocrystal of radius a~10*nm*, the ground state exciton binding energy is E_{ex}~1eV and quantized energy state is $E_{1,0}$~10meV. Thus, we can see a ~10^2 order of magnitude in the ratio of energies, pointing to a large effect of the exciton on absorption relative to the energy quantization effects.

The absorption spectra of these quantum dots exhibit exciton transitions as presented in Figure **4**(a) where the CuCl Bohr radius a_B is much less than the three semiconductor radii measured.

b. Intermediate Confinement Regime. The intermediate regime occurs when the exciton Bohr radius and semiconductor size are on the same order. The Bohr radius of electrons and holes are given by, $a_{(e,h)} = (\kappa\hbar^2)/(m_{e,h}e^2)$ where the electron effective mass is less than that of the hole, so we can expect $a_e > a > a_h$ in this regime.

The electron rapidly moves around the hole causing an average potential that confines the hole to move about the center of the quantum dot. The restrained hole acts as a donor, to the effect of a p-type dopant, located at the center of the quantum dot.

The absorption spectra of these quantum dots are shown in Figure **4**(b) where the CuBr Bohr radius is on the same order of the three quantum dot radii measured.

c. Strong Confinement Regime. The strong confinement regime occurs when the quantum dot radius a is smaller than the exciton Bohr radius a_B.

Again, turning to equation (13) the we can calculate the exciton binding energy and quantized energy by taking effective masses m_e=.17, m_h=.7, Bohr radius a_B=2.8*nm,* dot radius a=1*nm* and dielectric constant κ=5.3 for CdS, ground state calculations of exciton binding energy E_{ex} ~.6eV and quantized energy state $E_{1,0}$ ~2.7eV. Thus, we can see the exciton binding energy counteracts only a portion of the more significant quantized energy state and the absorption is shifted to higher energies.

It is in this regime that the confinement of a semiconductor can have a substantial energy/color absorption shift as calculated for CdS. This effect can be seen in Figure **4**(c) or more generally in Figure 5.

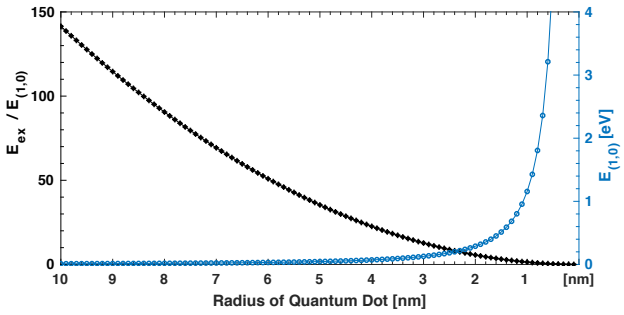

Figure 3. (Black) Ratio of ground state exciton binding energy E_{ex} to quantized state $E_{(1,0)}$ in CuCl (a_B=0.7*nm)* versus semiconductor radius a. (Blue) Quantized energy ground state $E_{(1,0)}$ to illustrate ~1/a^2 dependence.

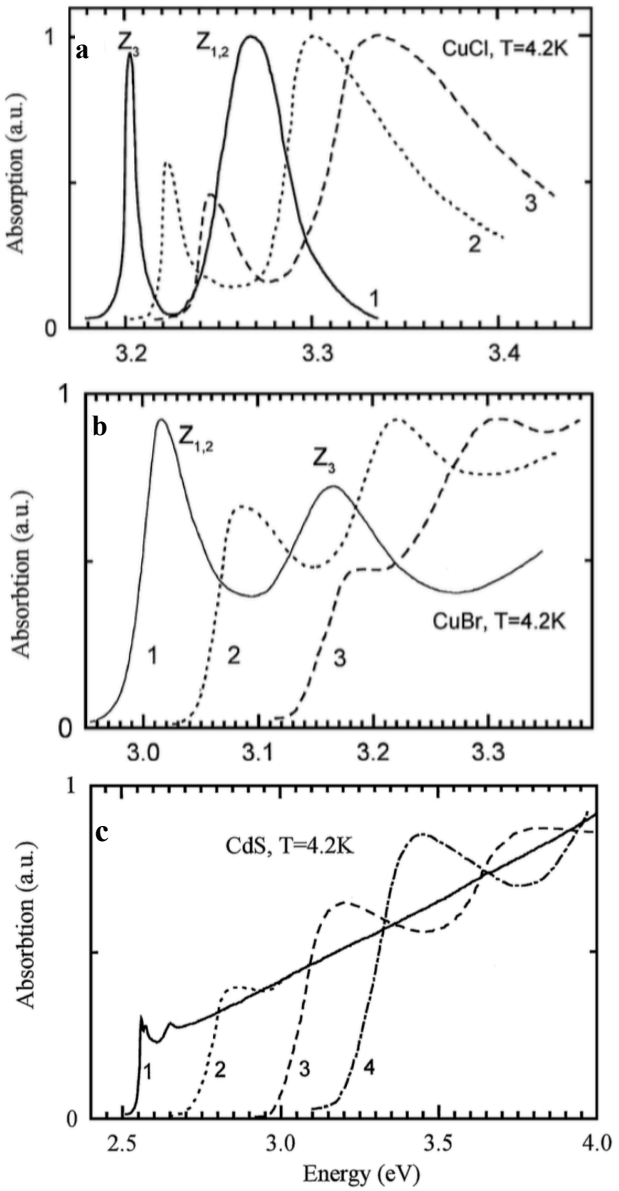

Figure 4. (a) Weak confinement: Absorption spectra of CuCl quantum dots of radii $a_{1,2,3}$ = 31, 2.9, 2.0*nm* and a_B = .7*nm*.
(b) Intermediate confinement: Absorption spectra of CuBr quantum dots with radii $a_{1,2,3}$ = 24, 3.6, 2.3*nm* and a_B = 1.8*nm*.
(c) Strong confinement: Absorption spectra of CdS quantum dots of $a_{1,2,3,4}$ = 33, 3.3, 1.5, 1.2*nm* and a_B = 2.8*nm*.[7]

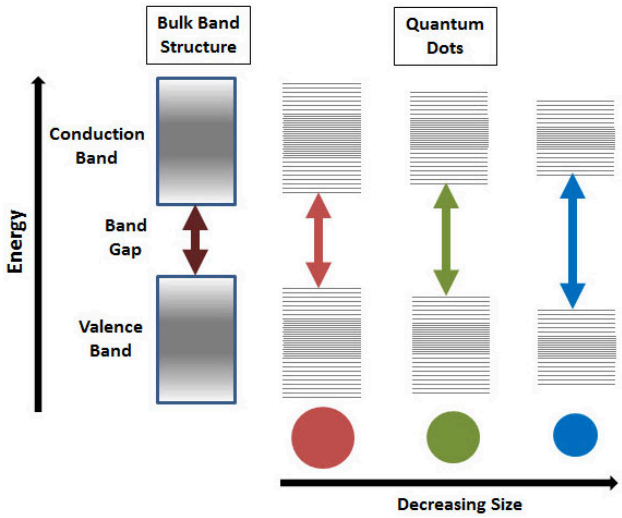

Figure 5. General schematic depicting the effect of spatial confinement on energy levels in quantum dots.

V. Conclusion

Although some semiconductor band gaps are larger than the visible spectrum in their bulk forms, experiments have shown the absorption and emission spectra of confined quantum dots can be tuned into the visible range by confining their radius. In this paper, we have addressed the energy quantization effects of confinement as well as the Wannier-Mott exciton on semiconductor absorption spectra.

VI. References

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