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DSE3T (Nano Materials and Applications)

Topic – Optical Properties (Part – 2)

We have already discussed part 1 of this e-report.

Now let us continue part 2 of it.

Quasi-Particles and Excitons:

When discussing the excitations in bulk systems, it has been common and extremely fruitful to introduce the notion of quasi-particles and subsequently of pairs and even groups of quasi-particles. This notion is useful only if their lifetime is long enough compared to the time characteristic of the experiment to be interpreted. Under these circumstances, a great advantage is that one can write an individual Schrödinger equation for this quasi-particle, leading to the GW approximation. One can also write a separate equation for a quasi-particle pair like an *exciton* (or *electron-hole pair*). Such an approach is presented here in detail, which is expected to remain useful for nanostructures down to relatively small sizes.

Basic Considerations. Experimental conditions to which the concept of quasi-particle fully applies occur when there is injection of one electron or one hole (extraction of one electron) into the system. This is the case in tunnelling experiments, for instance via a tip of a scanning tunnelling microscope, or in photo-emission (direct or inverse). Starting from an N electron neutral system, the lowest energy at which an electron can be injected is $E_c^{qp} = E(N+1) - E(N)$, where the index c denotes the lowest conduction state or unoccupied molecular orbital (or LUMO) and $E(N)$, $E(N+1)$ are the ground state energies of the N and $N+1$ electron systems. A similar situation occurs for holes, where we define the highest electron energy accessible to holes as $E_v^{qp} = E(N) - E(N-1)$, where the index v now denotes the highest valence state or occupied molecular orbital (or HOMO).

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Starting from a single particle calculation performed for the neutral N electron system, one can partition the quasi-particle energies as

$$E_c^{qp} = E_c^0 + \delta\Sigma_c \text{ and } E_v^{qp} = E_v^0 + \delta\Sigma_v$$

where, in the spirit of the GW approximation, E_c^0 and E_v^0 are the eigenvalues of the single-particle equations appropriate to the neutral N electron system, while $\delta\Sigma_c$ and $\delta\Sigma_v$ are the self-energy corrections.

Assuming that the particles are confined in the nanostructure, we separate each term into a bulk contribution and a correction due to the boundary conditions defining the nanostructure

$$E_c^{qp} = E_{c,bulk}^0 + \delta E_c^0 + \delta\Sigma_{c,bulk} + \delta\Sigma_{c,surf}$$

$$E_v^{qp} = E_{v,bulk}^0 + \delta E_v^0 + \delta\Sigma_{v,bulk} + \delta\Sigma_{v,surf}$$

where $E_{c,bulk}^0$ and $E_{v,bulk}^0$ stand for the bulk single-particle conduction and valence band limits, while δE_c^0 and δE_v^0 correspond to pure confinement effects.

Moreover, $\delta\Sigma_{c,bulk}$ and $\delta\Sigma_{v,bulk}$ stand for the corresponding bulk self-energy corrections whereas $\delta\Sigma_{c,surf}$ and $\delta\Sigma_{v,surf}$ are self-energies induced by the boundaries, i.e. surface corrections. Depending upon the choice, one can also group terms of the previous two equations in different ways, e.g.

$$E_c^{qp} = E_{c,bulk}^{qp} + \delta E_c^0 + \delta\Sigma_{c,surf}$$

$$E_v^{qp} = E_{v,bulk}^{qp} + \delta E_v^0 + \delta\Sigma_{v,surf}$$

where $E_{c,bulk}^{qp} = E_{c,bulk}^0 + \delta\Sigma_{c,bulk}$ and $E_{v,bulk}^{qp} = E_{v,bulk}^0 + \delta\Sigma_{v,bulk}$ are the exact quasi-particle bulk band limits. For the nanostructure *quasi-particle band gap* $E_g^{qp} = E_c^{qp} - E_v^{qp}$, we can thus write the corresponding expression as

$$E_g^{qp} = E_{g,bulk}^{qp} + \delta E_g^0 + \delta\Sigma_{g,surf}$$

where $\delta E_g^0 = \delta E_c^0 - \delta E_v^0$ and $\delta\Sigma_{g,surf} = \delta\Sigma_{c,surf} - \delta\Sigma_{v,surf}$.

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We come now to the *exciton* which can be created by optical excitation across the gap *inducing an electron-hole pair*. In a qualitative physical picture, the excitation energy will be equal to the quasi-particle gap E_g^{qp} corrected by the average value of the electron-hole pair Hamiltonian $\langle H_{eh} \rangle$. Therefore,

$$E_g^{exc} = E_g^{qp} + \langle H_{eh} \rangle$$

The electron-hole pair Hamiltonian H_{eh} can be written as the sum of two terms: (1) a kinetic energy term T due to the fact that the electron-hole wave function mixes excited quasi-particle states and (2) a potential energy term due to the screened Coulomb interaction between the two quasi-particles. This last contribution can again be split into two parts: (1) the direct electron-hole attraction $-\frac{e^2}{4\pi\varepsilon_0\varepsilon_{in}r_{eh}}$ (where r_{eh} is the inter-particle distance) and (2) the interaction between one of the quasi-particles with the image surface charge of the other. This term can be calculated as $-\frac{\alpha_{eh}}{4\pi\varepsilon_0 d}(\varepsilon_{in} - \varepsilon_{out})$, with d as the characteristic size of the nanostructure. Generally this term of the potential energy is much smaller compared to the 1st one. Therefore we get $E_g^{exc} = E_g^{qp} + \langle H_{eh} \rangle = E_g^{qp} + \langle T - \frac{e^2}{4\pi\varepsilon_0\varepsilon_{in}r_{eh}} \rangle$, which is the basic expression used in many simplified calculations.

Excitons in Direct Gap Semiconductors Nanocrystals:

Size-selective spectroscopic techniques such as resonant photoluminescence and photoluminescence excitation allow to get extremely detailed information on the lowest excitonic states of quantum dots or nanocrystals. This fine electronic structure is governed by the relative importance of different terms which constitute the Hamiltonian, such as confinement potential, spin-orbit interaction, Coulomb and exchange interactions. Each of these terms depends on quantum dot size in a different way. Two limiting situations can be considered: the weak confinement regime, when the dot size is larger than a few exciton radii and the strong confinement regime, when the quantum dot size is smaller than the exciton Bohr radius. In the latter regime, the confinement energy is much larger than the Coulomb interaction and both carriers are

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independently confined. However, even in this case, the Coulomb interaction exists since the electron and the hole are in a finite volume.

Tight binding configuration interaction calculations have been applied to the electronic structure of the lowest excitonic states in CdS nanocrystals with cubic lattice. Here CdS plays the role of a direct gap semiconductor. The nature of the predictions will be analyzed in a simplified effective mass picture in order to identify clearly the evolution from bulk to quantum dots. Fig. 1 summarizes this simple description of excitons in CdS quantum dots. Apart from the confinement effect, there are two terms in the Hamiltonian of a quantum dot which mainly determine the size dependence of its excitonic structure: the spin--orbit interaction and the electron-hole exchange interaction. Matrix elements of the spin-orbit interaction are constant. However the matrix elements of the electron-hole exchange interaction increase as the nanocrystal radius decreases. To understand the size dependence of the splittings between lowest exciton levels, one first considers two opposite limits: large and small dots.

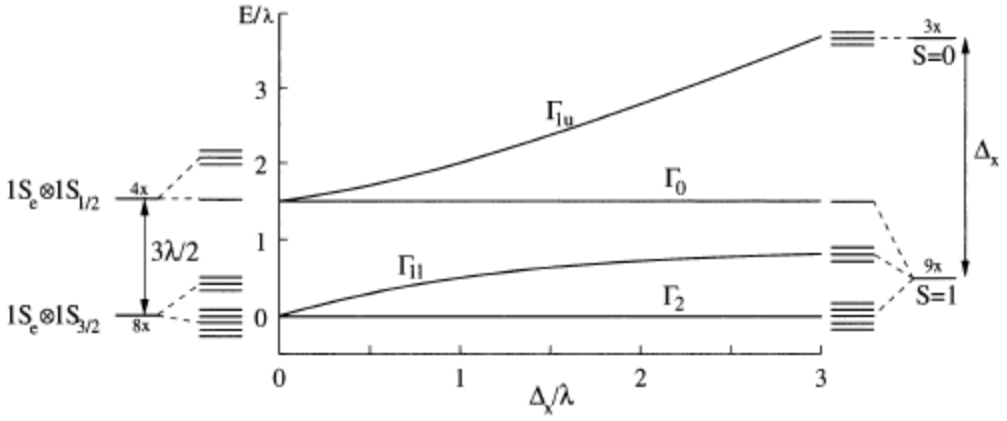

Fig. 1

For large dots, the lowest states converge to the classical situation of the bulk CdS, namely light and heavy-hole excitons and the spin-orbit split exciton. In this situation, the electron-hole exchange interaction is negligible with respect to the spin-orbit interaction. In this limit, the effective mass approximation becomes a powerful tool to calculate the electronic structure of spherical nanocrystals.

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The first electron level is the $1S_e$ state with twofold spin degeneracy and the first level of holes is the $1S_{3/2}$ state which is fourfold degenerate with respect to the hole angular momentum. The next hole level is $1S_{1/2}$ and its distance in energy from the $1S_{3/2}$ level is equal to $\frac{3\lambda}{2}$ where λ is the spin-orbit coupling parameter. Thus the lowest exciton state $1S_e \times 1S_{3/2}$ is eightfold degenerate and the next higher state $1S_e \times 1S_{1/2}$ is fourfold degenerate. The introduction in a perturbation scheme of the electron-hole exchange interaction splits the $1S_e \times 1S_{3/2}$ level into two groups of states. Since the total angular momentum J remains a good quantum number, the lowest exciton state, fivefold degenerate, is characterized by a momentum $J = 2$ and will be denoted hereafter as Σ_2. The upper exciton state, threefold degenerate, corresponds to a momentum $J = 1$ and will be denoted as Σ_{1l}. The higher exciton state $1S_e \times 1S_{1/2}$ is also split by the electron-hole exchange interaction into two groups of levels with $J = 0$ and $J = 1$, denoted as Σ_0 and Σ_{1u}, respectively. In the effective mass approximation, the value of the splitting is related to the electron-hole exchange energy Δ_x.

Excitons in Indirect Gap Semiconductors Nanocrystals:

We discuss here experimental data concerning the fine structure of optical spectra obtained for Si nanocrystals, which are indirect band semiconductors. All these experiments have been interpreted on the basis of a two-level model pictured on Fig. 2 with a spin triplet as the lowest excitonic state followed by a spin singlet.

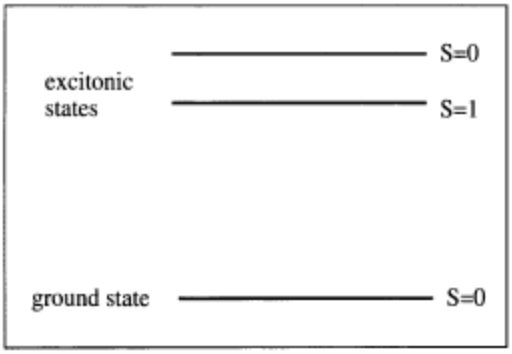

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Fig. 2

The two-level model proposed in the literature is based schematically on the fact that, from the spin-1/2 states of the electron and the hole, one can build one $S = 0$ and one $S = 1$ state. The energy splitting between these two states, due to the electron-hole exchange interaction, is expected to increase with confinement to reach values of order of 10 meV for crystallites of nanometer size. At low temperature, the excitons are mostly in the triplet state (Fig. 2) so that the radiative recombination time (from the $S = 1$ triplet exciton to the $S = 0$ ground state) would be infinite. However spin-orbit coupling slightly mixes the two states so that the recombination time is finite but very long. At higher temperature, the singlet excitonic state becomes populated and the luminescence lifetime decreases. On the other hand, for selectively excited luminescence at 2 K, the threshold in the excitation spectrum could be due to the fact that the excitons are photo-generated in the $S = 0$ state while the luminescence originates from the $S = 1$ state.

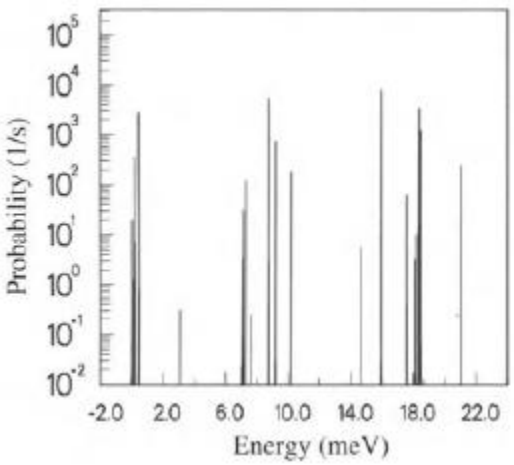

Fig. 3

Fig. 3 presents the calculated excitonic spectrum versus energy for a spherical crystallite. The spectrum is complex with many levels within 20 meV. This is due to the multiple degeneracies of the conduction and valence bands from which the exciton states are built. The energy intervals between these levels (~ 1 meV) are induced by the Coulomb and exchange terms and by inter-valley coupling. The lowest excitonic state is often characterized by a small radiative

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recombination rate but the states just above can have much more important rates. The relative homogeneity of these rates is due to the spin-orbit coupling. If this one is neglected, the $S = 1$ states would have an infinite lifetime. However, in silicon, the situation is quite different from this limiting case since the spin-orbit coupling constant ($\lambda = 15$ meV) is comparable in magnitude to the other couplings (Coulomb, inter-valley, exchange) so that all triplet and singlet states are mixed. Nevertheless, due to the exchange coupling, a general trend is observed that the lower states have on the average a lower recombination rate.

Quantitative Treatment of Excitons:

We now consider numerical calculations of the excitonic gap performed. Here we consider silicon crystallites as a test case. We express the excitonic gap E_g^{exc} as the difference between the quasi-particle gap E_g^{qp} and the Coulomb attractive interaction between these two quasi-particles E_{coul}.

$$E_g^{exc} = E_g^{qp} - E_{coul} = E_g^0 + \delta\Sigma - E_{coul}$$

Here $E_{coul} = -\langle H_{eh} \rangle$. E_g^{qp} is written as the sum of the independent particle value E_g^0 and the self-energy correction $\delta\Sigma$. We shall see that there is strong cancellation between the two large quantities $\delta\Sigma - \delta\Sigma_{bulk} = \delta\Sigma_{surf}$ and E_{coul}, such that $E_g^{exc} \approx E_g^0 + \delta\Sigma_{bulk}$. This justifies why the single particle calculations yield accurate results for E_g^{exc}.

Numerical Calculations. These calculations proceed in two steps: (1) by calculating the separate electron and hole quasi-particle energies via the GW method and (2) by determining the attractive Coulomb interaction between these quasi-particles. Such work has already been achieved with success from an ab initio point of view for bulk semiconductors, Na_4 clusters and small silicon clusters saturated by hydrogen atoms. However the computation is very time consuming and cannot be extended to nanocrystals. This is why the use of the tight binding formulation allows again to treat much larger clusters and get more information about the trends of E_g^{exc} with size.

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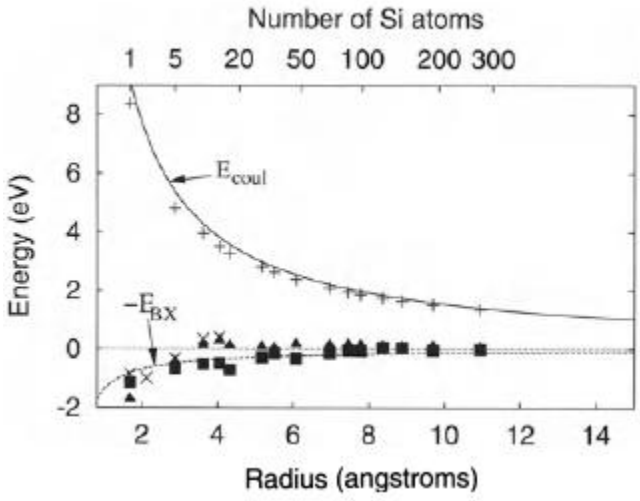

Fig. 4

We first consider the case of triplet states for which we can drop the exchange terms. As the excitonic states can be obtained from a diagonalization of an Hamiltonian, we have made apparent that E_c and E_v are the quasi-particle energies E_c^{qp} and E_v^{qp} obtained by the GW method. As for GW, these matrix elements are calculated in a tight-binding framework. The matrix equation is then diagonalized increasing the number of electron hole states till convergence is reached (this usually requires 10 electron and hole states). The lowest eigenvalue obtained in this way thus corresponds to the triplet exciton gap E_g^{exc}. The corresponding results are given on Fig. 4. However, it is more interesting to plot E_{coul} versus size, taken from the given equation as the difference $E_g^{qp} - E_g^{exc}$. On the same figure, the computed E_{coul} is also compared with the result of the classical electrostatic argument, where the effective interaction for the electron and hole at distance r_{eh} is the sum of two terms: a direct screened interaction plus the interaction of one particle with the polarization charge induced by the other. Taking the average of this with respect to the electron and hole distribution in the effective mass approximation gives (with $\varepsilon_{out} = 1$)

$$E_{coul} \approx \langle \frac{e^2}{4\pi\varepsilon_0\varepsilon_{in} r_{eh}} \rangle + \frac{\alpha_{eh}}{4\pi\varepsilon_0 R}(\varepsilon_{in} - \varepsilon_{out}) \approx (\frac{0.79}{\varepsilon_{in}} + 1)\frac{e^2}{4\pi\varepsilon_0 R}$$

which we plot on Fig. 4. The values for E_{coul} are extremely well approximated by the classical law.

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The figure also shows the difference $(\delta\Sigma - \delta\Sigma_{bulk}) - E_{coul}$ for the two extreme values of $\delta\Sigma - \delta\Sigma_{bulk}$ obtained. The latter are compared with the same quantity obtained from the full ab initio GW calculation for SiH_4, Si_5H_{12}, $Si_{10}H_{16}$ and $Si_{14}H_{20}$. The tight binding values fall in the same range as the ab initio values, especially those arising from the second LDA model. A striking feature displayed by Fig. 4 is that the quantities E_{coul} and $\delta\Sigma - \delta\Sigma_{bulk}$, while being pretty large, compensate each other to a large degree and, for clusters with $R > 0.6$ nm, the two quantities are practically identical so that their contributions to the excitonic gap cancel each other.

Charging Effects:

Single Particle Tunnelling Through Semiconductor Quantum Dots. We consider the tunnelling spectroscopy experiments on InAs nanocrystals performed by Banin et al. They reveal rich features due to the interplay between quantum confinement and charging effects. Here the conduction and valence band energy levels E_i^e and E_i^h of spherical InAs nanocrystals have been calculated with a sp^3 tight binding model with second nearest neighbour interactions. The calculations of the transport properties use an extension of the theory of Averin et al. and consider a standard double barrier tunnel junction (shown in Fig. 5). The system consists of two metallic electrodes El and E2 weakly coupled to a semiconductor quantum dot by two tunnel junctions J1 and J2 with capacitances C_1 and C_2. The metallic electrodes El and E2 are characterized by their Fermi energies $E_f^1 = E_f - eV$ and $E_f^2 = E_f$, where V is the bias voltage.

In terms of the junction capacitances C_1 and C_2, $U = \frac{e^2}{(C_1+C_2)}$ is the charging energy and $\eta = \frac{C_1}{(C_1+C_2)}$ is the part of the bias voltage (V) that drops across junction J2 in the neutral quantum dot. Tunnelling of an electron happens at the energy level E_i^e, symmetrically, hole tunnelling occurs at E_i^h. The current is calculated using the orthodox theory where one defines tunnelling rates through the junctions. At $T \to 0$ K, the $I(V)$ curve looks like a staircase. It exhibits a step each time E_f^1 or E_f^2 crosses a transition energy. A new charge state then

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becomes available in the quantum dot (addition step), or a new channel E_i^e or E_i^h is opened for tunnelling to a given, already available charge state (excitation step).

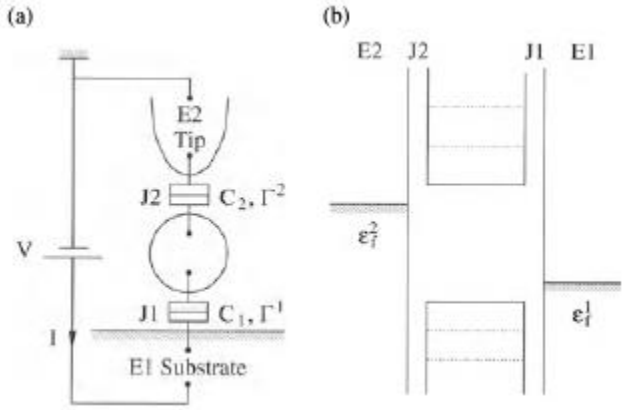

Fig. 5

This behaviour is apparent in the results. The differential conductance $G(V) = \frac{dI}{dV}$ is shown in Fig. 6 for an InAs nanocrystal 6.4 nm in diameter. The tip was retracted from the quantum dot so that $\frac{C_1}{C_2}$ is maximum and η is close to unity. A zero-current gap is observed around $V = 0$, followed by a series of conductance peaks for $V < 0$ and $V > 0$.

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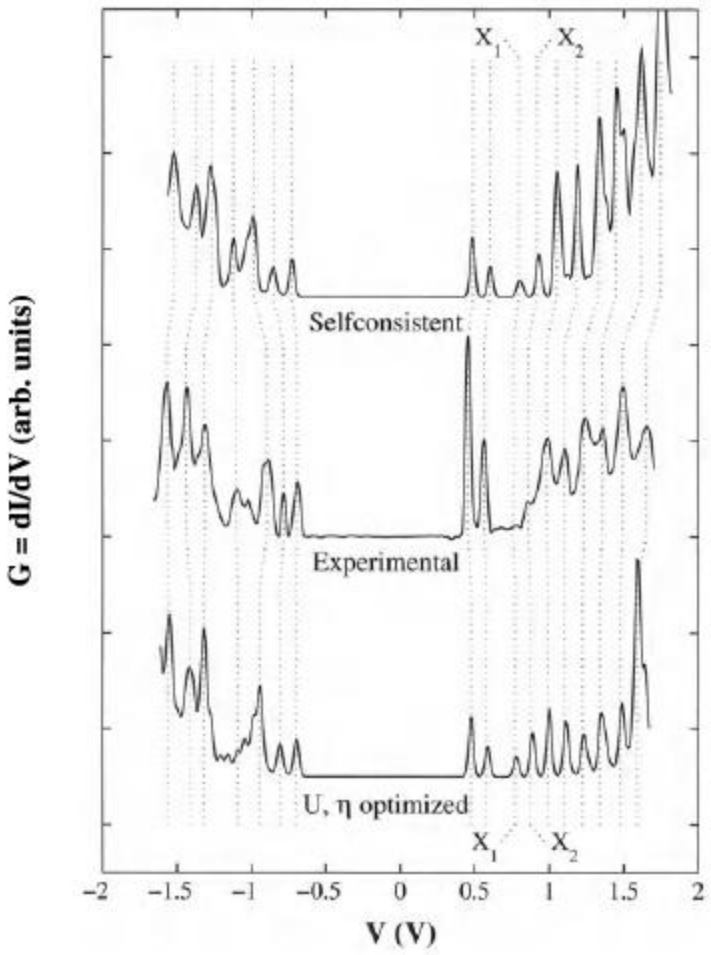

Fig. 6

This concludes part 2 of this e-report.

The discussion will be continuing in the part 3 of this e-report.

Reference:

Nanostructures: Theory and Modeling, C. Delerue & M. Lannoo, Springer

(All the figures have been collected from the above mentioned reference)