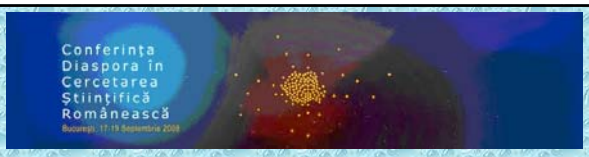

EFECTUL CONFINARII CUANTICE ASUPRA STRUCTURII ENERGETICE A SISTEMELOR CU DIMENSIONALITATE REDUSA

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CONTENT:

1. INTRODUCTION

Low dimensional system (LDS) ⇔ nanometric size on *at least* one direction.

Ratio between the number of atoms located at the surface/interface and the total number of atoms:

$$N_S^{(\delta)}/N = 2(3-\delta)a/d_\delta$$

δ – system dimensionality; a – interatomic distance; d_δ – (minimum) LDS size;
$N_S^{(\delta)}/N = 0.5$, $a \approx 0.25\ nm \Rightarrow d_0 = 3$ nm, $d_1 = 2$ nm, $d_2 = 1$ nm.

Surface/interface ⇔ potential barrier ⇔

wall of a quantum well ⇒ quantum confinement (QC)

- **QC – ZERO ORDER EFFECT**
  nature of the material – first order effect
  ➔*infinite* quantum well = first approximation

- **Shape of the quantum well ⇒ ratios between energies of consecutive levels ⇔ choice of the shape**
  ➔*rectangular* quantum well = good approximation

2. 2D SYSTEMS

Plane nanolayers

Hamiltonian splitting (exact):

- **parallel part – Bloch-type ⇒ 2D band structure;**
- **perpendicular part – infinite rectangular quantum well (IRQW) ⇒ QC levels**

➔ $$\varepsilon^{(2)} = \varepsilon_n\left(k_x, k_y\right) + \frac{2\pi^2\hbar^2}{m_\perp^* d^2} p^2, \quad p > 0.$$

$T = 0\ \mathrm{K} \Rightarrow \varepsilon_n(k_x, k_y) = E_y;\ E_{\mathrm{QC0}} = ?$ **By convention,** $E_{\mathrm{QC0}} \equiv 0.$

➔ $$\varepsilon^{(2)} = \left[\varepsilon_n\left(k_x, k_y\right) + \frac{2\pi^2\hbar^2}{m_\perp^* d^2}\right] + \frac{2\pi^2\hbar^2}{m_\perp^* d^2}\left(p^2 - 1\right)$$

$$\equiv \varepsilon_n^{(s)}\left(k_x, k_y\right) + \varepsilon_{p-1}.$$

QC levels located in the band gap!

- **Application: quantum well solar cells (QWSC)**

Matrix element of electric dipole interaction Hamiltonian:

$$H_{fi} = -\frac{2}{d} e \int_0^t \vec{E} \cdot \vec{r} \sin \frac{p_f \pi z}{d} \sin \frac{p_i \pi z}{d} dz \neq 0$$

$$\vec{E} = \vec{E}_{\parallel} \Rightarrow p_f = p_i; \ \vec{E} = \vec{E}_{\perp} \Rightarrow p_f - p_i = 2p - 1$$

$p_i = 1 \Rightarrow$ **internal quantum efficiency:** $\eta_{\perp} = \frac{4096 e^2}{\pi^2 c \hbar \varepsilon_0 \varepsilon_r^2} \cdot \frac{p^2 \sin^2 i}{\left(4p^2 - 1\right)^4}$

3. 1D SYSTEMS

Cylindrical nanowires

Hamiltonian splitting (approximate):

- **longitudinal part – Bloch-type ⇒ 1D band structure;**
- **transversal part – infinite rectangular quantum well (IRQW) ⇒ QC levels**

$$\rightarrow \ \varepsilon^{(1)} = \varepsilon_n(k_z) + \frac{2\pi^2 \hbar^2}{m_t^* d^2} x_{p,l}^2$$

$x_{p,l}$ – p-th non-null zero of cylindrical Bessel function $J_l(x)$

$T = 0\ \mathrm{K} \Rightarrow \varepsilon_n(k_z) = E_v;\ E_{QC0} = ? \Rightarrow E_{QC0} \equiv 0.$

$$\rightarrow \varepsilon^{(1)} = \left[\varepsilon_n(k_z) + \frac{2\pi^2\hbar^2}{m_t^* d^2} x_{1,0}^2 \right] + \frac{2\pi^2\hbar^2}{m_t^* d^2} \left(x_{p,l}^2 - x_{1,0}^2 \right)$$

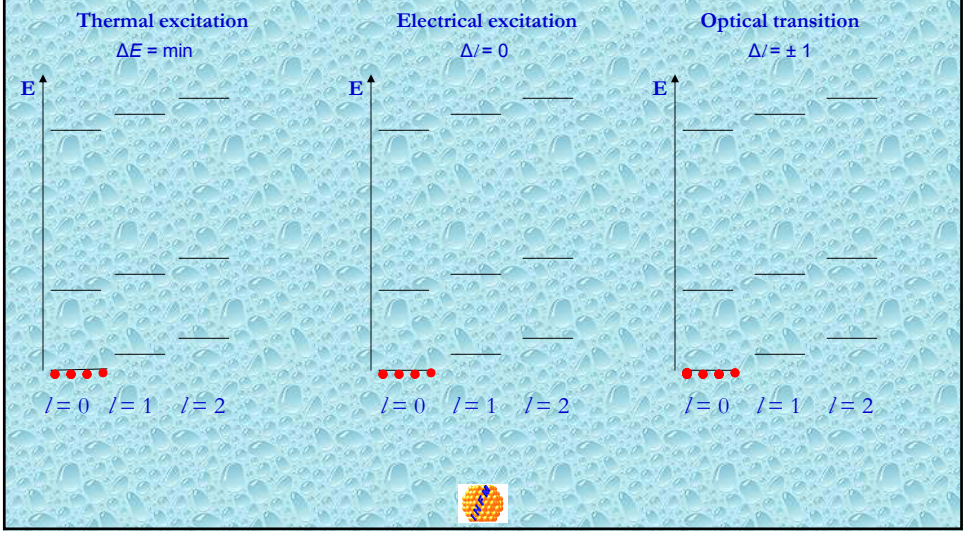
$$\equiv \varepsilon_n^{(s)}(k_z) + \varepsilon_{p-1,l}, \quad l \text{ – orbital quantum number.}$$

QC levels located in the band gap!

Valence band = particle reservoir ⇒
excitation transitions start from the fundamental level
➔ activation energy ratio

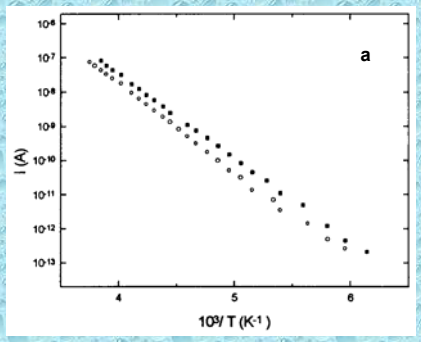
$$R_{nw} = \frac{x_{p''+1,l''}^2 - x_{1,0}^2}{x_{p'+1,l'}^2 - x_{1,0}^2}$$

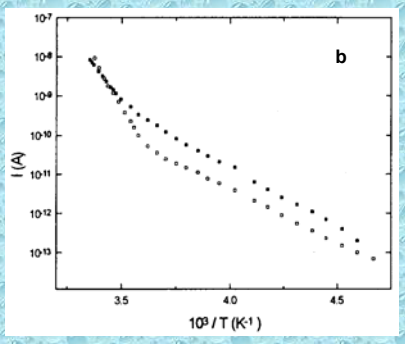
Thermal transition ⇔ $\Delta\varepsilon$ = minimum;
Electrical transition ($eU >> k_B T$) ⇔ $\Delta l = 0$;
Optical transition ⇔ $\Delta l = \pm 1$.



Application: nc-PS

- $I - T$ characteristics $\Rightarrow \Delta l = 0$.





a – fresh sample; activation energy:
$E_1 = 0.52 \pm 0.03$ eV

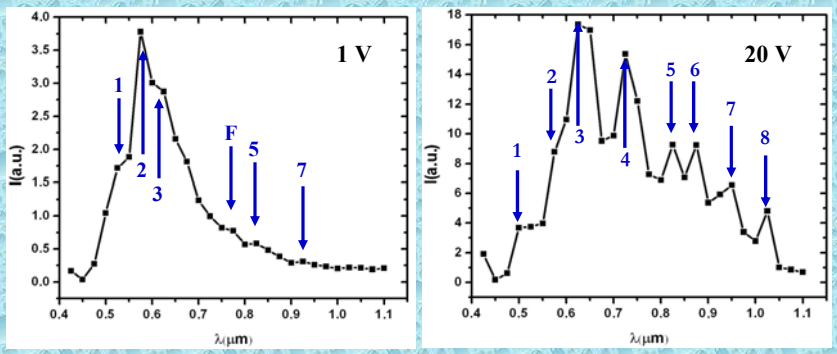
EMA: $\varepsilon \sim d^{-2} \Rightarrow d_f = 3.31 \pm 0.03$ nm;
LCAO: $\varepsilon \sim d^{-\alpha}$, $\alpha = 1.02 \Rightarrow d_f = 3.40 \pm 0.03$ nm.

b – stabilized sample; activation energies:
$E_1 = 0.55 \pm 0.05$ eV, $E_2 = 1.50 \pm 0.30$ eV;
$E_2/E_1 = 2.727$

➔ $E_1 = \varepsilon_{1,0}$, $E_2 = \varepsilon_{2,0}$;
$d_s = 3.22 \pm 0.05$ nm.

Application: nc-PS

➢ $I-\lambda$ characteristics $\Rightarrow \Delta l = \pm 1$.



No.	1	2	3	4	F	5	6	7	8
λ (nm)	504	574	629	717	761	827	873	932	1025
E (eV)	2.46	2.16	1.97	1.73	1.63	1.50	1.42	1.33	1.21

QC transitions identified in nc-PS:

nc-PS	No.	E_{exp} (eV)	Transition
PT spectral maxima	1	2.46	(2, 1) → (3, 2)
	2	2.16	(0, 0) → (2, 1)
	3	1.97	(1, 1) → (3, 0)
	4	1.74	(0, 2) → (2, 1)
	5	1.50	(0, 2) → (1, 3)
	6	1.42	–
	7	1.33	(0, 1) → (2, 0)
	8	1.21	(0, 1) → (1, 2)
PL	1	1.89	(1, 1) → (2, 2) (1, 1) → (3, 0)
TDDC	1	0.55	(0, 0) → (1, 0)
	2	1.50	(0, 0) → (2, 0)

$$\sigma_r = E_{\exp} / E_{theor} - 1, \ |\sigma_r| \le 5\ \%.$$

4. 0D SYSTEMS

Spherical nanodots – quantum dots

➢ $d \leq 5$ nm $\Rightarrow$ **no more bands $\Leftrightarrow$ groups of energy levels = quasibands**

➔ $$\varepsilon^{(0)} = \frac{2\pi^2\hbar^2}{m^* d^2} x_{p,l}^2$$

$x_{p,l}$ – p-th non-null zero of spherical Bessel function $j_l(x)$

$T = 0$ K $\Rightarrow \varepsilon^{(0)} = E_v$; $E_{QC0} = ? \Rightarrow E_{QC0} \equiv 0$.

➔ $$\varepsilon^{(0)} = \frac{2\pi^2\hbar^2}{m^* d^2} x_{1,0}^2 + \frac{2\pi^2\hbar^2}{m^* d^2}\left(x_{p,l}^2 - x_{1,0}^2\right) \equiv E_V + \varepsilon_{p-1,l}$$

l **– orbital quantum number.**

QC levels located in the quasiband gap!

EMA: $\varepsilon \sim d^{-2}$
LCAO: $\varepsilon \sim d^{-\alpha}, \alpha = 1.39$

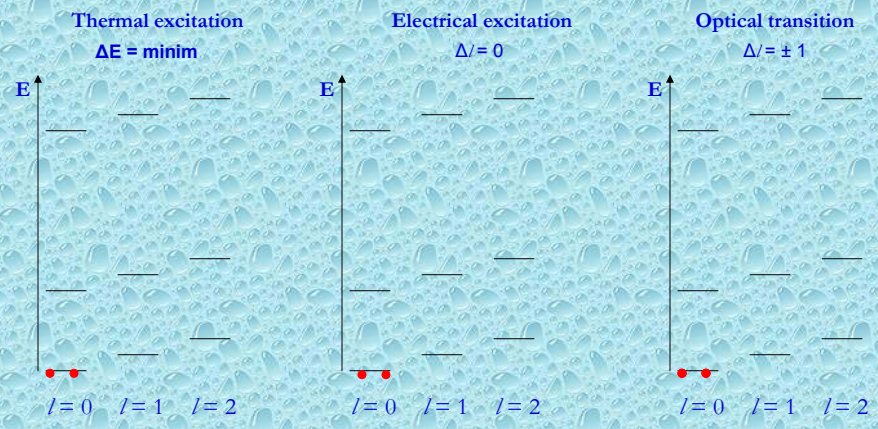
➔ $m^* \approx m_\infty^* + \frac{a}{d}\left(m_{0e} - m_\infty^*\right)$

➔ $m^* \approx m_{0e}$ **for quantum dots**

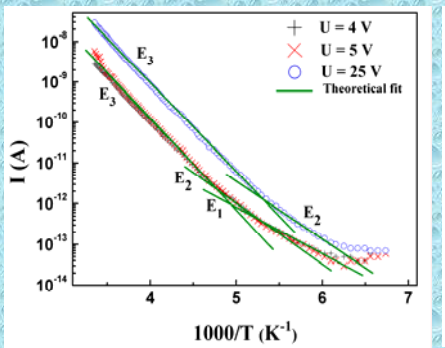
No more proper VB = no more particle reservoir
⇒ excitation transitions: from the last occupied level to the next one ↱ selection rules

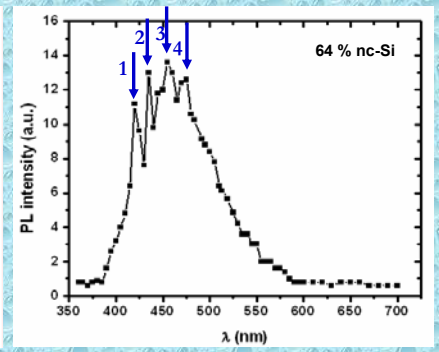
➔ $R_{qd} = \frac{x^2_{l'',p''+1} - x^2_{l',p'+1}}{x^2_{l',p'+1} - x^2_{l,p+1}}$

Thermal transition ⇔ $\Delta\varepsilon$ = minimum;
Electrical transition $(eU >> k_B T)$ ⇔ $\Delta l = 0$;
Optical transition ⇔ $\Delta l = \pm 1$.



➢ Application: Si – SiO_2





I – T characteristics ⇒ $\Delta l = 0$

$E_1 = 0.22 \pm 0.02$ eV
$E_2 = 0.32 \pm 0.02$ eV
$E_3 = 0.44 \pm 0.02$ eV

PL spectrogram ⇒ $\Delta l = \pm 1$

No.	1	2	3	4
λ (nm)	415	436	571	479
E (eV)	2.99	2.85	2.71	2.59

QC transitions identified in Si – SiO_2

Si – SiO_2	No.	E_{exp} (eV)	Transition
PL (d = 4,92 nm)	1	2,99	(1, 2) → (6, 1)
	2	2,85	(0, 1) → (5, 2)
	3	2,71	(1, 1) → (6, 0)
	4	2,59	(1, 1) → (5, 2)
TDDC (d = 5,28 nm)	1	0,22	(0, 1) → (1, 1)
	2	0,32	(1, 1) → (2, 1)
	3	0,44	(2, 1) → (3, 1)

$|\sigma_r| < 3\ \%$

5. CONCLUSIONS

- **Allmost ALL the energies measured in electrical transport, phototransport and photoluminescence ⇔ transitions between QC levels.**
  Different quantum selection rules ⟶ different energy levels.

- **Differences between model and experiment due to:**
  - ✓ **size distribution;**
  - ✓ **shape distribution;**
  - ✓ **finite depth of the quantum well.**

THANK YOU FOR YOUR ATTENTION!