Dielectrically confined excitons and polaritons in natural superlattices – perovskite lead iodide semiconductors

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We present the results of calculations of excitonic binding energies, wave functions, diamagnetic factors, and polariton reflection spectra for perovskite lead iodide compounds – naturally grown semiconductor/insulator multi-quantum-well superlattices, with taking into account the interaction of electrons and holes with self-image charges, the image-potential-mediated Coulomb interaction, and the inhomogeneity of electric-field configuration.

Currently there is a great deal of interest in naturally grown superlattices — lead iodide based layered semiconductors $(C_nH_{2n+1}NH_3)_2PbI_4$, $n = 4, 6, 8, 9, 10, 12$ [abbreviated as C_n - PbI_4] and $(C_6H_5-C_2H_4NH_3)_2(CH_3NH_3)_{m-1}Pb_mI_{3m+1}$, $m = 1, 2$ [abbreviated as PhE - PbI_4 ($m = 1$) and PhE - Pb_2I_7 ($m = 2$)]¹⁻⁵. This interest is accounted for by the strong excitonic effects in these substances, which make them promising new materials for optoelectronics. Exciton binding energies as large as $E_{ex} = 320$ meV and pronounced polarization-dependent excitonic polariton effects were reported³.

Lead iodide perovskite compounds may be regarded² as natural semiconductor/insulator multi-quantum-well (S/I MQW) superlattices (SLs) consisting of semiconductor lead iodide layers sandwiched between insulator barrier alkylammonium layers (whose gap is twice as large as that of the lead iodide layers). It was shown in²⁻⁴ that the exciton enhancement in these natural S/I MQWs may be attributed to alternating semiconductor and insulator layers with considerably different dielectric constants, causing the image-potential-mediated modification of electron-hole (e-h) interaction and so-called dielectric confinement of excitons⁶.

In the present paper we calculate the exciton parameters in lead iodide compounds taking into account their SL structure and the image potential including the self-image corrections (arising due to the interaction of electrons and holes with their own image charges). Describing the superlattice structure of the compounds, we follow the Guseinov's approach⁷. As to the self-image terms, we include them into the QW localizing potential, thus renormalizing the QWs states.

Our calculation evolves two successive steps: (i) we find the MQW one-electron and one-hole wavefunctions of perpendicular motion with accounting for the interaction with self-image charges, and (ii) solve Schrödinger equation for in-plane excitonic wave-function with averaged (over MQW wave-functions) image-potential-mediated Coulomb interaction.

We assume the excitonic state is of a Wannier-Mott type. This assumption can be self-consistently verified: the calculated mean e-h distance in an exciton a_{ex} is large compared to the interatomic distance a_0 (about 12 and 3–6 Å, respectively). However, we have to ascertain

that the Wannier-Mott condition $a_{\text{ex}} \gg a_0$ is on the verge of its validity. In our calculations we are using envelope-function approximation (EFA) conventional for SLs and MQWs⁹. The only distinction from the known theory is allowing for the image potentials. Our point when choosing the material parameters of S/I layers is to use that of PbI_2 (for semiconductor layers) and of structurally close organic material (for insulator layers), as it was done in⁴. The detailed description of our calculation procedure see in Ref.¹⁰.

Table 1 shows certain known material parameters of lead iodide compounds, of PbI_2 and organic materials $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ and $\text{C}_6\text{H}_5\text{-C}_2\text{H}_4\text{NH}_2$, along with the results of our calculations of excitonic binding energies E_{ex} , radii a_{ex} , and diamagnetic factors c_0 .

We have chosen $\text{C}_{10}\text{-PbI}_4$ as a starting point in our calculations and fitted our theory to the experimental values of E_{ex} and c_0 , shown in Tab.1. When fitting, we have mostly used two adjustable parameters: the ionic radius of iodide atoms R_I , which we added (following^{3,4}) to the geometric width of the PbI_4 layer l_w^0 (shown in Tab.1), $l_w = l_w^0 + 2R_I$, $l_b = l_b^0 - 2R_I$ and reduced excitonic mass μ . We have also assumed the dielectric constant of well layers $\varepsilon_w = 6.1$ (see Tab.1) and chosen that of barrier layers ε_b from the condition $\varepsilon_\infty = [\varepsilon_w l_w + \varepsilon_b l_b]/[l_w + l_b]$. Thus we have guaranteed the correct experimental value of high frequency dielectric constant ε_∞ . As a rule, calculated in such a way ε_b is close to that shown in Tab.1 for $\text{C}_n\text{H}_{2n+1}\text{NH}_2$.

We have obtained better agreement with the experimental values of E_{ex} and c_0 choosing $\mu = 0.21m_0$ and $R_I = 1 \text{ \AA}$. After fitting our theory to the experimental data on $\text{C}_{10}\text{-PbI}_4$, we have calculated the excitonic parameters in other lead iodide compounds, using the same $\mu = 0.21m_0$ and $R_I = 1 \text{ \AA}$, $\varepsilon_w = 6.1$ and changing accordingly to Tab.1 $l_{w,b}^0$, ε_∞ (when the latter is known). The results of our calculations of E_{ex} , c_0 and a_{ex} are shown in Tab.1. One can see that although our fitting procedure was rather crude and the number of unknown material parameters was large, theoretical results show reasonable agreement with the experimental data for the whole lead iodide family. The fact that our theory gives different excitonic parameters for different members of C_nPbI_4 family, clearly demonstrates the role of SL structure. (Within our approach the well layers are the same for all C_nPbI_4 compounds.) Our accounting for self-image corrections, which is another difference of our approach from the previous one⁴, manifests itself in larger fitted value for reduced excitonic mass ($\mu = 0.21m_0$ in our calculations and $0.1m_0$ in⁴).

The polarization-resolved optical experiments^{2,3} using EM wave with frequency close to the polariton resonance show a large difference in light reflection for two polarizations of electromagnetic wave $\vec{E} \perp \vec{c}$ and $\vec{E} \parallel \vec{c}$ (where $\vec{c}$ is a normal to layers of the superlattice). This seeming anisotropy of the exciton oscillator strength may be explained by essentially different spatial configurations of the electric field in the S/I SLs for these two polarizations. If $\vec{E} \perp \vec{c}$, the electric field is uniform, whereas at $\vec{E} \parallel \vec{c}$ the electric field in well layers (just where the excitons are confined to) is much smaller than in the barrier ones, thus causing a decrease of excitonic oscillator strength. It is also clear, that for $\vec{E} \parallel \vec{c}$ polarization the exciton-photon interaction has to depend drastically on the exciton wavefunction.

The results of our calculations of the polariton reflection spectra within the nonlocal theory of Ref.¹¹ are illustrated in Fig.1. Note a drastic reflectivity dependence on the exciton formfactor for $\vec{E} \parallel \vec{c}$ polarization. The reflection spectra for $\vec{E} \perp \vec{c}$ polarization does not depend on the exciton formfactor at all.

Table 1: Experimental and calculated parameters of lead iodide compounds: high-frequency dielectric constant ϵ_∞ , band gap E_g , S/I layer width l_w^0/l_b^0 , exciton binding energy, diamagnetic factor and mean radii E_{ex} , c_0 and a_{ex}

Compound	ϵ_∞	E_g	l_w^0	l_b^0	E_{ex}		c_0		a_{ex}
		eV (T=1.6 K)	Å	Å	meV		$10^{-7} \frac{eV}{T^2}$		Å
					exp	theor	exp	theor	theor
PbI ₂	6.1 ^c	2.53 ^b			30 ^b 63 ^e		9.7 ⁱ		40 ^b 19 ^e
C _n H _{2n+1} - NH ₂	2.1 ^d (n=10) 2.07 ^h	5.5 ^g (n=12)							
C ₆ H ₅ - C ₂ H ₄ NH ₂	2.34 ^h								
C ₄ -PbI ₄			6.36 ^k	8.53 ^g 8.81 ⁱ	290 ± 20 ^g	289 [†]		1.48 [†]	11.9 [†]
C ₆ -PbI ₄			6.36 ^k	10.03 ^l		285 [†]	2.16- 3.53 ^a	1.60 [†]	12.3 [†]
C ₈ -PbI ₄			6.36 ^k	12.02 ^l		288 [†]		1.70 [†]	12.7 [†]
C ₉ -PbI ₄			6.36 ^k	13.53 ^l	320 ± 30 ^g	293 [†]		1.70 [†]	12.7 [†]
C ₁₀ -PbI ₄	3.24 ⁱ	2.87 [†]	6.36 ^k	14.89 ^l	320 ± 30 ^g	301 ^{††}	1.7 ⁱ	1.68 ^{††}	12.7 ^{††}
C ₁₂ -PbI ₄	3.39 ^k		6.36 ^k	18.15 ^k	310 ± 30 ^g	317 [†]		1.63 [†]	12.5 [†]
PhE-PbI ₄	4.41 ^k	2.58 ^k	6.36 ^k 6.41 ^j	9.82 ^k 9.85 ^j	220 ± 30 ^k	269 [†]		1.60 [†]	12.4 [†]
PhE-Pb ₂ I ₇		2.30 ^k	12.70 ^k 13.05 ^j	9.71 ^j	170 ^k	223 [†]		1.95 [†]	13.6 [†]

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Fig.1 The reflection spectra of the S/I SL for 30° angle of incidence (a) and beam directed along the SL layers (b) calculated for three different exciton formfactors $\psi_{exc}(z_e = z_h = z, \rho = 0)$, shown in the inset.

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