Electronic properties of three- and low-dimensional semiconducting materials with Pb halide and Sn halide units

Electronic properties of three- and low-dimensional semiconducting materials with Pb halide and Sn halide units

I B Koutselas†, L Ducasse‡ and G C Papavassiliou†

† Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantine Avenue, 11635, Athens, Greece
‡ Laboratoire de Physicochimie Théorique, Université Bordeaux 1, Unité de Recherche associéeau CNRS 503, Domaine Universitaire, 33045 Talence Cédex, France

Abstract. Band-structure calculations, semiempirical as well as *ab initio*, have been applied to study the electronic band gap of the new exotic natural low-dimensional MX systems (where M = Pb or Sn and X = I, Br or Cl). Moreover, variational calculations are employed to calculate the excitonic binding energies, whose amplification is due not only to the quantum confinement of the excitons but also to a dielectric enhancement effect. A single set of semiempirical parameters is sought to describe the materials; comparison of the calculations with experimental data shows this to be successful in the case of the PbI- and PbBr-containing compounds.

In recent years, artificial systems, mainly low-dimensional (LD) systems, have been developed which have novel physical characteristics with applications in the future nanoelectronics industry [1]. In addition to artificial structures, synthetic crystalline three-dimensional (3D) and LD systems with metallic or semiconducting behaviour have been prepared and studied [2–10]. In the special case where the active material has semiconducting behaviour, these artificial systems not only are interesting in themselves but are also characterized by enhanced excitonic binding energy E_b and enhanced oscillator strength with respect to the corresponding 3D systems [1]. The latter properties identify these compounds as efficient non-linear optical elements or as light-emitting diodes that can be tuned at different wavelengths by the choice of the semiconducting compound.

In this paper, we are going to focus on synthetic 3D and LD (i.e. two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D) semiconducting materials that have lead halide or tin halide units as their basic building block. In particular, we present theoretical calculations in comparison to experimental results, which concern energy gaps and excitonic binding energies for 3D, 2D (quantum well), 1D (quantum wire) and 0D (quantum dot) molecular structures.

The building block of the materials, which will be presented, is the MX_6 octahedron, where M = Pb or Sn and X = I, Br or Cl. In the 3D compounds with formula $CH_3NH_3MX_3$ [3], each octahedron shares all its corners with neighbours to form a 3D network (figure 1(a)). Contrary to the structurally isomorphic $CsMX_3$ [3], whose Cs atom occupies the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ position in the cubic lattice, the methylammonium cation C_1 is disordered. The 2D materials are of the form $(C_9H_{19}NH_3)_2MX_4$ [4] (figure 1(b)) or similar compounds which have

different ammonium cations, such as $C_6H_5CH_2CH_2NH_3(C_{6-2})$ instead of nonylammonium C_9 [5]. In these compounds, each octahedron shares four coplanar corners with neighbours, forming separate infinite layers which are held far from each other with the help of the long C_9 amine. Each layer has a thickness L_{well} of about 6.34 Å. Similarly, in the 1D compound $(NH_2C(I) = NH_2)_3PbI_5$ [6, 7], each octahedron shares two opposite corners with neighbours, forming separate infinite chains. Each chain has a diameter $2R$ of about 6.4 Å (figure 1(c)). The 0D compound has the chemical formula $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ [8] and consists of isolated (non-interacting) octahedra (figure 1(d)). All these compounds have been found to be semiconductors and all the structures depicted in figure 1 form at room temperature.
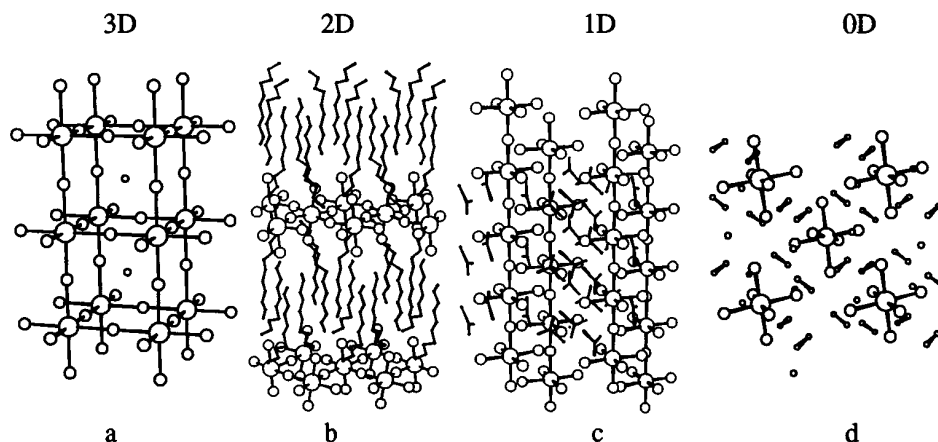

Figure 1. Crystal structures of (a) $CH_3NH_3PbI_3$, (b) $(C_9H_{19}NH_3)_2PbI_4$, (c) $(NH_2C(I)=NH_2)_3PbI_5$ and (d) $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ where large spheres are Pb atoms, medium spheres I atoms, and small spheres O, N and C atoms.

In addition, compounds whose dimensionality lies between 2D and 3D will also be described [2, 9, 10]. These are layered compounds containing n layers of the original 2D structure, with $n = 2, 3, 4, \ldots$. Compounds involving the C_9 or the C_{6-2} ammonium cations with $n \geqslant 3$ have not yet been prepared in single-crystal form.

It has been observed that the excitonic absorption, luminescence, photoluminescence excitation and photoconductivity bands are shifted to higher energies as the dimensionality of the compounds is decreased [2]. Also, it has been observed that the excitonic binding energy increases as the dimensionality is decreased [2].

Band-structure calculations have been performed for these compounds by using the formalism of the extended Hückel theory (EHT) [11, 12]. X-ray crystallographic data were used to describe the unit cells, which do not have any type of disorder except in the case of the 2D compounds involving the C_{6-2} amine. In the latter cases, a larger unit cell was adopted, which has a composition of slightly distorted octahedra, so that the in-plane halide atoms have an occupancy factor of 0.5. Only the outer valence s and p orbitals were used for the semiempirical calculations.

Figure 2 shows the calculated electronic band structures for some of the above compounds, along certain high-symmetry directions of the Brillouin zone. The bands shown include the four bands below the Fermi level and the four bands above the Fermi level

(except for the 3D case where only three bands exist). The parameters, ionization energy H_{ii} and STO exponent ζ, which were used are given in table 1 (for the PbI compounds).
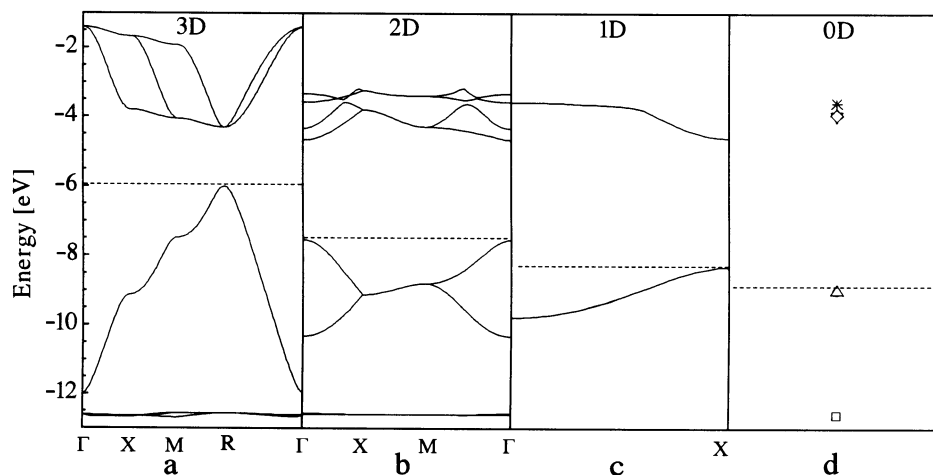

Figure 2. Electronic band structures of (a) $CH_3NH_3PbI_3$, (b) $(C_9H_{19}NH_3)_2PbI_4$, (c) $(NH_2C(I) = NH_2)_3PbI_5$ and (d) $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$: $- - -$, the position of E_{Fermi}.

Table 1. The parameters H_{ii} and ζ for the PbI compounds.

Orbital	H_{ii}	ζ
Pb 6s	−15.7	2.350
Pb 6p	−8.0	2.060
I 5s	−18.0	2.679
I 5p	−12.7	2.482

The eight parameters in table 1, which were used in the EHT calculations, were taken from literature tables [12] and have been kept constant, except for the I 5p exponent, which originally had the value $\zeta(I\ 5p) = 2.322$. This parameter was allowed to vary in order to obtain close agreement between the calculated band gap and the experimental band gap in the case of the 3D PbI network. Effort was made to ensure that the minimum number of parameters varied from their literature values in order to simplify the modelling of the electronic properties of the relevant compounds.

It should be noted that the EHT calculations, except for the 3D case, were performed both with and without the amines, and in both cases the 2D, 1D and 0D band gaps did not change. In all cases, calculations showed that the compounds are direct-gap semiconductors. In the 3D case, calculations neglecting C_1 show a direct gap to appear at the R point. Calculations involving the amine have not been performed since the amine is disordered and there are many different orientations that it could attain. However, it is known that the 3D PbX compounds, where X = Br or Cl, which have formed either with Cs or with C_1, exhibit excitonic peaks at almost the same energies [2, 13]. Moreover, the appearance of the band gap at R is in agreement with the calculation in [13]. Thus, we expect that band-structure calculations with Cs will yield useful results for describing the C_1 case. Indeed,

the direct gap at R does not change, and a new indirect gap of 1.28 eV appears between the R point and the M point, since the conduction bands have a lower energy at the M point with the introduction of the Cs atom. The parameters used for the Cs atom were H_{ii}(Cs 6s) $= -3.88$ eV, H_{ii}(Cs 6p) $= -2.49$ eV and ζ(Cs 6s) $= \zeta$(Cs 6p) $= 1.06$ [12]. In particular, the compositions of the conduction and valence bands do not change appreciably at the R point with the inclusion of the Cs atom; however, at the M point we have the same valence band in contrast with a conduction band with an appreciable contribution from the Cs 6p orbitals. This effect is under investigation as well as *ab-initio* calculations for the band gap of the 3D compounds, as will be discussed later. In all cases, the conduction band is composed primarily of an antibonding Pb 6p–I 5s orbital, where the valence band is mainly an antibonding Pb 6s–I 5p orbital (at least for the set of the above parameters).

In the 3D (isotropic) semiconductors based on Pb halides the excitons have been considered to be Wannier like and thus the well known formulae

$$E_b = 13.6 \frac{\mu}{\varepsilon^2} \,(\text{eV}) \tag{1}$$

and

$$r_B = 0.529 \frac{\varepsilon}{\mu} \,(\text{Å}) \tag{2}$$

can be used in order to compute the binding energy E_b and the Bohr radius r_B of the excitons (where ε is the background dielectric constant and μ the reduced electron–hole pair mass). For C_1PbI_3, ε was found to be 6.5, from reflectance spectra [14]. This value has also been used to describe the 2D layers and the 1D wires (namely $\varepsilon_{well} = \varepsilon_{wire} = 6.5$) of other PbI systems.

The excitonic binding energy has also been calculated for the 2D and 1D systems, considering that the excitons are Wannier like. In all cases the effective reduced masses were obtained from the electronic band structure. The 2D systems are made out of alternating layers of well (MX) and barrier (amine) material. In these natural 2D systems, the barrier material has a significantly smaller dielectric constant than the well material and that causes profound changes in the electronic properties of the 2D systems since the electrostatic energy of an electron–hole pair can be increased through the image charges induced on the barrier. This effect is manifested by a dramatic increase in E_b [15]. The exciton is considered to be Wannier like. The calculations of E_b were performed by incorporating the exact solution for the potential induced by a point charge inside a periodic dielectric multilayer system [16]. The barrier and well have been modelled by dielectric constants which are constant and isotropic. The electron–hole pair is assumed to exist in a specific well only, since the barrier has a large energy gap and long length so that it prevents the exciton from moving in another well†. The motion of the exciton is also modified by the fact that the layer is a periodic system. In particular, from the band-structure calculations the reduced excitonic masses were found to be $\mu = 0.09$, 0.12 and 0.07 for the 3D, 2D and 1D systems, respectively. Finally, the complete energy spectrum of the exciton is described by non-linear integral equations, which give rise to singularities in the case when the particle wavefunctions tunnel into the barrier or are quite complex in mathematical form. For these reasons, a simple trial wavefunction was chosen for variational calculations. It is worthwhile pointing out that the equations governing a point-charge-induced potential in a periodic dielectric multilayer system require careful limiting procedures in all extreme cases, such as integrating at large wavenumbers or having the ratio $L_{well}/L_{barrier}$ very large

---

† It should be pointed out that the barrier of these 2D systems does not absorb in the region of the excitonic spectral region, as has been verified by optical experiments.

or small. Calling $\phi_k(z, z_q)$ the Fourier transform of the potential at z (the z axis being perpendicular to the layer) which is produced by a point charge q located at z_q (z_q in a specific well of the multilayer system), then the actual electron–hole potential energy is

$$\phi(\mathbf{r}_e, \mathbf{r}_h, z_e, z_h) = \frac{1}{4\pi} \int J_0(k|\mathbf{r}_h - \mathbf{r}_e|)k(q_e\phi_k(z_e, z_h) + q_h\phi_k(z_h, z_e))\, dk$$

where ϕ_k depends on ε_{well} and on $\varepsilon_{well}/\varepsilon_{barrier}$ [16]. Here $J_0(x)$ is the Bessel function of the first kind of integral order 0. In particular, the form of ϕ_k for $L_{barrier} \to \infty$ is

$$\phi_k(z, z_q) = \frac{2\pi q}{k\varepsilon_{well}}\left(\exp(-k|z - z_q|) + \frac{2\lambda}{\zeta^4 - \lambda^2}\{\zeta^2 \cosh[k(z + z_q)] + \lambda \cosh[k(z - z_q)]\}\right)$$

where

$$\zeta = \exp\left(\frac{kL_{well}}{2}\right) \qquad \lambda = \frac{\varepsilon_{well} - \varepsilon_{barrier}}{\varepsilon_{well} + \varepsilon_{barrier}}.$$

The two-body Hamiltonian can be expressed as

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{\hbar^2}{2m_e}\frac{d^2}{dz_e^2} - \frac{\hbar^2}{2m_h}\frac{d^2}{dz_h^2} + \phi(\mathbf{r}_e, \mathbf{r}_h, z_e, z_h)$$

where the translation energy has been assumed to be zero. Using the variational principle with the trial wavefunction, defined only for z_e, z_h in a particular well,

$$\psi(z_e, z_h, r) = \sqrt{\frac{8}{\pi r_2^2 L_{well}^2}} \exp\left(-\frac{r}{r_2}\right) \sin\left(\frac{\pi z_e}{L_{well}}\right) \sin\left(\frac{\pi z_h}{L_{well}}\right)$$

where $r = |\mathbf{r}_e - \mathbf{r}_h|$ and r_2 is a free parameter, E_b was calculated. The maximum value of

$$E = -\langle \psi|\hat{H}|\psi\rangle \tag{3}$$

where

$$\langle \psi|\psi\rangle = 1$$

as a function of r_2 is the binding energy of the exciton; then the corresponding r_2 is the exciton's 2D Bohr radius r_B. We should point out that with the choice of this trial wavefunction the kinetic energy terms perpendicular to the layer motion (along the z axis) vanish, as they include no fitting parameters (since the energy of an electron–hole pair has these z-dependent terms whether or not the attracting pair has dissociated into two free particles). In the appendix the binding energy equation for the periodic Hamiltonian is given, for completeness, and is used in this paper. Again, for the case when $L_{barrier} \to \infty$, the energy takes the following form, assuming a simple trial function of the above form (the formula is given here to illustrate the dependence of E_b on λ):

$$E_b = -\frac{\hbar^2}{2\mu r_2^2} + \frac{8q_e^2}{r_2\varepsilon_{well}} \sum_{n=-\infty}^{\infty} \lambda^{|n|}\xi(n, r_2)$$

where $\xi(n, r_2) \geqslant 0$ for *all* n, r_2 and

$$\xi(n, r_2) = \int_0^\infty \exp(-u) \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \frac{[\cos(\pi x)\cos(\pi y)]^2\, du\, dx\, dy}{\sqrt{1 + (16L_{well}^2/r_2^2 u^2)(x - (-1)^n)y - n)^2}}.$$

In the simple case when $L_{well} \to 0$ and $\lambda = 0$ we derive, upon maximization, the well known $E_b(2D) = 2\mu e^4/\hbar^2\varepsilon_{well}^2$ (see [1]).

Comparing figure 2 and the experimental data from [2, 7], which are summarized in table 2, one can see that the theoretical calculations predict that, by decreasing the

dimensionality of the PbI network, the band gap increases, as well as the binding energy of the lowest exciton. It also predicted that the excitonic Bohr radius decreases. In all cases, the agreement between experiment and theory is more than qualitative, and the values of the excitonic Bohr radii confirm the initial approximation for describing the exciton as of Wannier type. It should be noticed that, for an idealized 2D system, without dielectric confinement (i.e. $\varepsilon_{well}/\varepsilon_{barrier} = 1$), $E_b(2D) = 4E_b(3D)$ (assuming that the well thickness approaches zero) [17]. This limiting case is approached by modern artificial structures such as GaAs/Al$_x$Ga$_{1-x}$As multilayers systems (for example [106] in [1] and references therein). For $(C_9)_2PbI_4$†, $\varepsilon_{well}/\varepsilon_{barrier} = 3.53$, and then one finds that $E_b(2D) = 13E_b(3D)$. For these calculations, $E_b(3D) = 29$ meV, $\varepsilon_{barrier} = 1.84$ (determined as in [18]) are considered.

Table 2. Calculated values, for the PbI systems, of the band gap E_g, the lowest exciton's binding energy E_b and the excitonic Bohr radius r_B; the room-temperature experimental results are given in parentheses.

Compound	Dimensionality	E_g (eV)	E_b (meV)	r_B (Å)
$(C_1)_1PbI_3$	3D	1.70[a] (1.70)[b]	29[c] (30)[b] (45)[d]	38[c]
$(C_1)_3(C_9)_2Pb_4I_{13}$	2D (four layer)	2.07[a] (2.03)[b]	130[e] (60)[b]	22.9[e]
$(C_1)_2(C_9)_2Pb_3I_{10}$	2D (three layer)	2.19[a] (2.17)[b]	161[e] (96)[b]	20.5[e]
$(C_1)_1(C_9)_2Pb_2I_7$	2D (two layer)	2.37[a] (2.38)[b]	218[e] (181)[b] ($\geqslant$ 220)[d]	17.5[e]
$(C_9)_2PbI_4$	2D (one layer)	2.85[a] ($\geqslant$ 2.82)[b]	377[e] ($\geqslant$ 388)[b] ($\geqslant$ 330)[d]	12.4[e]
$(NH_2C(I){=}NH_2)_3PbI_5$	1D	3.67[a] ($\geqslant$ 3.10)[b]	715[f] ($\geqslant$ 410)[b]	15.5[g]
$(C_1)_4PbI_6 \cdot 2H_2O$	0D	5.04[a] (3.87)[b]	— (545)[b]	—

[a] From [11] with parameters from [12] (except that $\zeta = 2.482$ for the I 5p orbital, in order to get the best fit to the experimental results of the 3D system); in all cases the PbI networks were taken into account; crystallographic data from [3] (Pb–I, 3.1642 Å) and [8] Pb–I, 3.153 Å) for the 3D system; crystallographic data from [4] (Pb–I, 3.194–3.206 Å) for 2D (one layer) and intermediate values for the other 2D systems (i.e. four layer → 3.18 Å, three layer → 3.185 Å and two layer → 3.19 Å); crystallographic data from [6] (Pb–I, 3.153–3.287 Å) for the 1D system; crystallographic data from [8] (Pb–I, 3.195–3.231 Å) for the 0D system.
[b] From the optical absorption spectra in [2].
[c] From equations (1) and (2) in text.
[d] From the temperature dependence of photoluminescence intensities in [19].
[e] From a modified theory from [16], as in the text.
[f] Method described in this paper (see text).
[g] This is the value for r_1 described in the text.

The calculations concerning the $n = 2, 3, 4$ compounds were performed by creating artificial layered structures, where the Pb–I distances were varied so that the large n compounds have layers that are similar to the 3D compound. Calculated and experimental results [2, 19] for these compounds are summarized in table 2. In the $n > 1$ systems, band-structure calculations showed that the excitonic mass is changing for the different n-layer systems but stays between those of 2D and 3D compounds. So, the reduced excitonic mass was considered to have an average value of 0.107. However, the change in binding energy upon changing μ from 0.09 (3D value) to 0.12 (2D value) increases E_b by 20 meV and decreases the Bohr radius by 1 Å for the $n = 2, 3, 4$ systems, which shows that the assumption for the μ-value is valid. One expects that the properties of the 2D systems with large n approach those of the corresponding 3D systems (see table 2).

For the $(C_{6-2})_2PbI_4$ compound, the interatomic distances Pb–I are 3.15–3.2 Å. Calculations of the energy gap gave $E_g = 3.0$ eV, while the experimental value is 2.58 eV.

† The 3D excitonic radius is 38 Å; such a well of 6.5 Å thickness is a very good approximation to a real 2D system.

Moreover, the binding energy for this system was found to be 191 meV and $r_B = 14.2$ Å, for $\mu = 0.16$ (obtained from band-structure calculations); the corresponding experimental value of E_b is 220 meV [2]. Here, $\varepsilon_{barrier}$, determined as in [18], was estimated to be 3.05. Therefore, for this system, $\varepsilon_{well}/\varepsilon_{barrier} = 2.13$ and $E_b(2D) = 6.58E_b(3D)$. In other words, the binding energy of the system is smaller than that of the $(C_9)_2PbI_4$ system as a result of the dielectric confinement effect [15].

The Hamiltonian for the layered compounds involves three unknown parameters, i.e. the dielectric constant of the well, the dielectric constant of the barrier and the mass of the exciton. It has been assumed that the iodine atoms facing the barrier define an interface plane at which the wavefunction goes to zero and is the interface at which the well's edge is defined. Theoretically, if there is a physical reason for such an interface plane, it may be at varying distance from the iodine plane. In previous investigations [2, 18, 20] the effective mass and dielectric constant of PbI_2 were used or the exciton mass was used as a fitting parameter in a simpler model of an exciton in a dielectric well. The well's dielectric constant is not well known, since the well is not related to any 3D structure, on which one could perform reflectance experiments nor is it easy to perform theoretical calculations on such an atomic-like layer since the matrix elements necessary to calculate the dielectric constant are not known. Finally, better results in the case of wide wells could have been obtained if the z dependence was included in the exponential form of the trial wavefunction. There is also some uncertainty in the experimental determination for the E_b-values of 2D systems, especially for $n = 3, 4$, because these compounds have not yet been prepared in single-crystal form.

For the 1D case the exciton was assumed to be formed inside a cylinder whose radius R is defined by the edges of the octahedra. The dielectric confinement due to the surrounding material was also included, assuming that the barrier has infinite thickness. The Hamiltonian for this system has the form [21]

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{\hbar^2}{2\mu}\frac{d^2}{dz^2} - \frac{q_e^2}{\varepsilon_{chain}\sqrt{r_e^2 + r_h^2 - 2r_er_h\cos(\theta_e - \theta_h) + z^2}}$$
$$+\frac{2q_e^2}{\pi}\left(\frac{1}{\varepsilon_{chain}} - \frac{1}{\varepsilon_{barrier}}\right)$$
$$\times \sum_{m=-\infty}^{\infty}\int_0^\infty C_m(k)\cos(k(z_e - z_h))I_m(kr_h)I_m(kr_e)\cos[(\theta_h - \theta_e)m]\,dk$$

where

$$C_m(k) = \frac{K_m(kR)K_m'}{I_m(kR)K_m' - I_m'K_m(kR)\varepsilon_{chain}/\varepsilon_{barrier}}$$

and

$$K_m' = \left.\frac{d(K_m(kr))}{dr}\right|_{r=R} \qquad I_m' = \left.\frac{d(I_m(kr))}{dr}\right|_{r=R}.$$

Here ε_{chain} is the dielectric constant of the chain of PbI octahedra, and I_m and K_m are the modified Bessel functions of the first and second kinds, respectively, of integral order m. Using the variational principle with a trial wavefunction of the form

$$\psi(z_e, z_h, r_e, r_h) = B\exp\left(-\frac{z^2}{r_1^2}\right)\cos\left(\frac{\pi r_e}{2R}\right)\cos\left(\frac{\pi r_h}{2R}\right) \qquad B^2 = \sqrt{\frac{2}{\pi}}\frac{8\pi^3}{R^4r_1(\pi^2 - 4)^2}$$

where r_1 is a free parameter, the following equation can be derived for the binding energy of this exciton:

$$
\begin{aligned}
E_b = {}& -\frac{\hbar^2}{2\mu r_1^2} + \frac{q_e^2 4\sqrt{2^7 \pi^5}}{\varepsilon_{chain} r_1 (16 - 8\pi^2 + \pi^4)} \\
& \times \int_0^1 \int_0^1 \int_0^\pi \int_0^\infty \frac{[\cos(\pi r_e/2)\cos(\pi r_h/2)]^2 r_e r_h \exp(-2z^2 R^2/r_1^2)\, \mathrm{d}r_e\, \mathrm{d}r_h\, \mathrm{d}\theta\, \mathrm{d}z}{\sqrt{r_e^2 + r_h^2 - 2 r_e r_h \cos\theta + z^2}} \\
& + \frac{32\pi^3 q_e^2}{R(\pi^2 - 4)^2}\left(\frac{1}{\varepsilon_{barrier}} - \frac{1}{\varepsilon_{chain}}\right) \\
& \times \int_0^\infty C_0\left(\frac{u}{R}\right)\exp\left(-\frac{r_1^2 u^2}{8R^2}\right)\left[\int_0^1 I_0(r_e u) r_e \cos^2\left(\frac{\pi r_e}{2}\right)\mathrm{d}r_e\right]^2 \mathrm{d}u.
\end{aligned}
\tag{4}
$$

The results for the 1D system were obtained by considering that the dielectric constant of $NH_2C(I)=NH_2$ is the same as that of C_{6-2} (i.e. 3.0). The model used for calculating the 1D binding energy includes the following approximations: the dielectric constant of the chain is the same as that of the 3D compound, and the exciton is Wannier like. The results are summarized in table 2. One can see that E_b for the 1D system is much higher than those for 3D systems. It should be noted that the binding energy of an idealized 1D system is infinite [17]†.

Excitonic binding energy calculations for the 0D compound (with metal halide units) could be evaluated with methods similar to those applied for molecules or clusters [22]. Such results are not discussed here. It should be noted that the calculated and experimental band gaps do not agree very well for this compound. It is well known that the tight-binding approximation works well in 'tight' systems and also that atomic systems with large interatomic distances exhibit pronounced correlation effects. This is the case with the 0D compound where the Pb–I distances are the largest in this series of compounds. Thus it is expected that the correlation effects (not included in the semiempirical method) can be a source of disagreement for the two values of E_g in table 2 and such an effect cannot be analysed within the semiempirical domain (especially with a single-zeta basis).

Similar calculations have been performed for the PbBr compounds, where crystallographic data and sufficient absorption spectra were available; these are summarized in table 3.

There are not sufficient experimental data for similar compounds with PbCl units or Sn halide units. However, in the case of the $(C_{6-2})_2 SnI_4$ (2D) system, considering the experimental parameters of SnI_2, the E_b- and r_B-values have been calculated, as well as for similar systems $(C_{10})_2 SnI_4$ and $(C_1)(C_{6-2})_2 Sn_2 I_7$; the results are in good agreement with the experimental data [2]. Unfortunately, a single set of semiempirical parameters has not been found for the whole series of SnI systems, so that the optical band gaps and excitonic binding energies can be compared with the experimental data.

Thus, it should be noted that there are sets of experimental data [23] concerning the $C_1 SnX_3$ compounds, where X = Br or I, which are not completely understood or explained in terms of the semiempirical band-structure approach presented in this paper, such as the pseudo-metallic properties. Also, discrepancies arise in the calculated band structures of the 3D compounds. In particular, LMTO calculations [24] for the $CsSnBr_3$ system and LCAO calculations [13] for $CsPbBr_3$ predict different forms of band gap transition, since the former predicts a transition at M (due to a forbidden transition at R) and the latter, as well as this

---

† If the experimental gap was fitted by changing the ζ for the I 5p orbital, then $\mu = 0.04\, m_e$. This would have lowered the binding energy to about 560 meV.

Table 3. Calculated values, for the PbBr systems, of the band gap E_g, the lowest exciton's binding energy E_b and the excitonic Bohr radius r_B; the room-temperature experimental results are given in parentheses.

Compound	Dimensionality	E_g (eV)	E_b (meV)	r_B (Å)
$(C_1)_1PbBr_3$	3D	2.470[a] (2.48)[b]	— (150)[b]	1.45[c]
$(C_9)_2PbBr_4$	2D (one layer)	— (3.87)[b]	897[d] (733)[b]	6.2[d]
$(C_{6-2})_2PbBr_4$	2D (one layer)	3.89[a] ($\geqslant$ 3.49)[b]	610[d] ($\geqslant$ 430)[b]	7[d]

[a] As in footnote to table 2 except that $\zeta = 2.339$ for the Br 4p orbital, in order to get the best fit to the experimental results of the 3D system; in all cases the PbBr networks were taken into account; crystallographic data in [28] (Pb–Br, 2.951 Å) for 3D systems; crystallographic data in [29] for the $(C_{6-2})_2PbBr_4$ 2D system (Pb–Br, 3 Å). The parameters that were used for the models in the text are $\varepsilon_{3D} = 3.29$, with $\mu = 0.12$ and 0.2 for the 3D and 2D systems, respectively. The width for the C_9 system has been assumed to be 6 Å.

[b] From the optical absorption spectra in [2].

[c] From equations (1) and (2) in text.

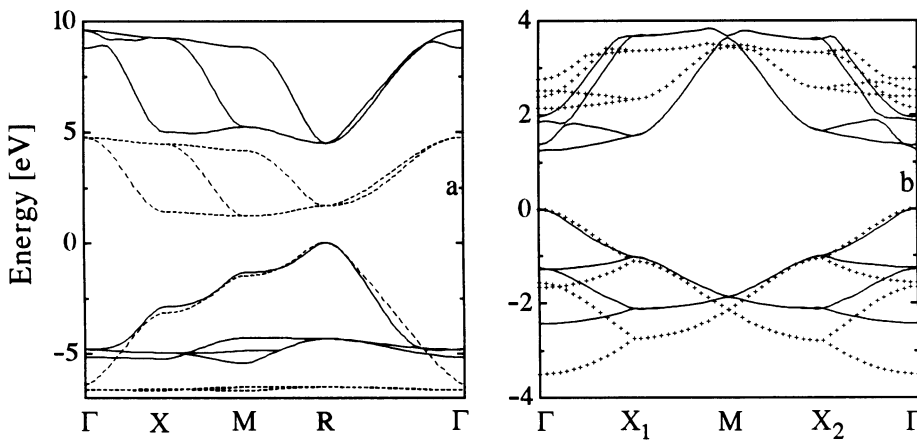[d] From a modified theory from [16] as in the text.

Figure 3. Electronic band structures of (a) $CH_3NH_3SnI_3$ and (b) $(C_6H_5CH_2CH_2NH_3)_2SnI_4$: ——, *ab-initio* Hartree–Foch LCAO calculations; – – –, +, EHT calculations, where $\zeta(I\ 5p) = 2.47$ and 2.38 for (a) and (b), respectively, so as to fit the experimental band gap. The energy of all calculations are shifted by E_{Fermi}.

paper, predicts a direct band gap at R, since the conduction and valence wavefunctions at this point have different parities.

Finally, *ab-initio* calculations have been performed on some of these LD systems, currently with the Hartree–Fock LCAO method which is distributed as the program package described in [25]. The description of the unit cells has been attained by using the *ab-initio* effective core pseudopotentials and 1s–1p pseudo-basis of [26]. Spin–orbit coupling was not taken into account, although the pseudopotentials had been created using a relativistic Hamiltonian. The calculations were performed on the 3D and 2D SnI systems, in order to test the results of the semiempirical results. The band gaps are found to be different when compared with the experimental data, probably because of correlation effects which

are not computed in the *ab-initio* program. This result is well known in Hartree–Fock approaches; for example Palmer and Ladik [27] use a Moller–Plesset treatment of the correlation energy in polyparaphenylene to reduce a Hartree–Fock band gap of 8.7–2.3 eV, with the experimental value being 2.8 eV. The basis set which is really optimized for molecular calculations rather than for periodic systems probably does not play an important role in this case. Nevertheless one can see in figures 3(a) and 3(b) for the 3D and 2D systems, respectively, that the band widths and the trends in the conduction and valence bands are very similar for the two different methods. The bands shown in figure 3 are again the four bands below the Fermi level and the four bands above the Fermi level. It should be noted that the energies of the bands in the figures have been shifted by E_{Fermi}. The relative positions of the bands with large band widths compared to the flat bands indeed vary between the two sets of calculations. This may be ascribed to the effect of self-consistency whose role depends on the types of band. However, the flat bands are rather low in energy with respect to the Fermi energy and do not play a significant role in the physics of the compounds (this is also the case for the bottom valence bands which are not shown here). For the 3D system a Cs atom was taken into account instead of the methylammonium atom.

In conclusion, a methodology has been pursued to explain consistently the energy of the band gap and excitonic binding energy in the new LD systems.

Appendix

The binding energy of an exciton which exists in the well region of a periodic dielectric multilayer quantum well system will be presented. It has been derived by the formalism described in the text, i.e. using equation (3), where all integrations except that in k-space have been carried out. The well thickness and dielectric constant are L_{well} and ε, respectively. The barrier thickness and dielectric constant are $L_{barrier}$ and ε_1, respectively. The equation has been divided up for convenience. We define

$$\alpha = \frac{1 + \varepsilon_1/\varepsilon}{2} \qquad \beta = 1 - \alpha \qquad g_1 = \frac{2\alpha^2}{2\alpha - 1}$$

$$x = 1 + (g_1 - 1)\tanh(kL_{barrier})\tanh(kL_{well}) \qquad y = \sqrt{x^2 - (\mathrm{sech}(kL_{barrier})\,\mathrm{sech}(kL_{well}))^2}$$

$$f_- = \alpha + \beta \frac{\sinh(k(L_{barrier} - L_{well}))}{\sinh(k(L_{barrier} + L_{well}))} \qquad f_+ = \alpha - \beta \frac{\cosh(k(L_{barrier} - L_{well}))}{\cosh(k(L_{barrier} + L_{well}))}$$

$$t1 = \frac{\sinh(kL_{well}/2)xf_+}{yf_-} \qquad t7 = -\cosh\left(\frac{kL_{well}}{2}\right)\tanh(k(L_{barrier} + L_{well}))$$

$$t17 = \frac{32\pi^4(\alpha - \beta)\sinh(kL_{well}/2)(t1 + t7)}{\tanh(k(L_{barrier} + L_{well}))}$$

$$t2 = -2\sinh^2\left(\frac{kL_{well}}{2}\right)\{1 - 2\alpha\beta[1 + \cosh^2(kL_{barrier})]\} \qquad t3 = (\alpha - \beta)^2\sinh^2\left(\frac{kL_{well}}{2}\right)$$

$$t4 = -2(\alpha - \beta)^2 x \cosh(kL_{well})\left[\cosh(kL_{barrier})\sinh\left(\frac{kL_{well}}{2}\right)\right]^2$$

$$t5 = \cosh(kL_{well})\sinh^2\left(\frac{kL_{well}}{2}\right)((\alpha^2 + \beta^2)\cosh(2kL_{barrier}) - 2\alpha\beta)$$

$$t6 = 2(\alpha - \beta)\sinh(2kL_{barrier})\cosh\left(\frac{kL_{well}}{2}\right)\sinh^3\left(\frac{kL_{well}}{2}\right)$$

$$t8 = \frac{(\alpha - \beta)(3(kL_{well})^5 + 20\pi^2(kL_{well})^3 + 32kL_{well}\pi^4)}{2}$$

$$td = \cosh(kL_{barrier})\cosh(kL_{well})\sinh(k(L_{barrier} + L_{well}))$$

$$td_1 = \frac{yf_-}{16\pi^4} \qquad td_2 = kL_{well}(kL_{well})^2 + 4\pi^2)$$

$$F(k) = \frac{\pi[(t2 + t3 + t4 + t5 + t6)/td_1 td + t17 + t8]}{td_2^2 \varepsilon_1}.$$

Then

$$E_b = -\frac{\hbar^2}{2\mu r_2^2} + \frac{4q_e^2}{r_2 \pi} \int_0^\infty \frac{F(2k/r_2)}{(k^2 + 1)^{3/2}} \, \mathrm{d}k.$$

References

[1] See, e.g., Weisbuch C and Vinter B 1991 *Quantum Semiconducting Structures* (London: Academic)
    Chemla D S 1993 *Phys. Today* June 46
[2] Papavassiliou G C, Koutselas I B, Terzis A and Raptopoulou C P 1995 *Microcrystalline and Nanocrystalline Semiconductors (Mater. Res. Soc. Symp. Proc. 358)* (Pittsburgh, PA: Materials Research Society) p 283, and references therein
    Papavassiliou G C and Koutselas I B 1995 *Synth. Met.* **71** 1713
[3] Poglitch A and Weber D 1987 *J. Chem. Phys.* **87** 6373 and references therein
[4] Nagapetyan S S, Dolzhenko Yu I, Arakelova E R, Koshkin V M, Struchkov Yu T and Shklover V E 1988 *Russ. J. Inorg. Chem.* **33** 2806
[5] Papavassiliou G C, Koutselas I B, Terzis A and Whangbo M H 1994 *Solid State Commun.* **91** 695
[6] Wang S, Mitzi D B, Feild C A and Guloy A 1995 *J. Am. Chem. Soc.* **117** 5297
[7] Lagouvardos D J, Koutselas I B and Papavassiliou G C 1995 unpublished
[8] Vincent B R, Robertson K N, Stanley Cameron T and Knop O 1987 *Can. J. Chem.* **65** 1042
[9] Papavassiliou G C, Koutselas I B and Lagouvardos D J 1993 *Z. Naturf.* b **48** 1013
[10] Mitzi D B, Feild C A, Harrison W T A and Guloy A M 1994 *Nature* **369** 467
[11] Whangbo M H and Hoffmann R 1978 *J. Am. Chem. Soc.* **100** 6093
[12] Alvarez S 1989 Table of parameters for extended Hückel calculations *Report* Universitat de Barcelona
[13] Heidrich K, Kunzel H and Treusch J 1978 *Solid State Commun.* **25** 887
    Heidrich K, Schäfer W, Schreiber M, Söchtig J, Trendel G, Treusch J, Grandke T and Stolz H J 1981 *Phys. Rev.* B **24** 5642
[14] Hirasawa M, Ishihara T and Goto T 1994 *Physica* B **201** 423
[15] Hanamura E 1988 *Optical Switching in Low-dimensional Systems (NATO ASI Series 194)* ed H Haug and L Banyai (New York: Plenum)
[16] Guseinov R R 1984 *Phys. Status Solidi* b **125** 237
[17] He X F 1991 *Phys. Rev.* B **43** 2063
[18] Hong X, Ishihara T and Nurmikko A V 1992 *Phys. Rev.* B **45** 6961
[19] Ishihara T 1994 *J. Lumin.* **60–1** 269
    Papavassiliou G C 19 unpublished
[20] Gippius N A, Muljarov E A, Tikhodeev S G, Ishihara T and Keldysh L V 1994 *Mater. Res. Soc. Symp. Proc. 328)* (Pittsburgh, PA: Materials Research Society) p 775
[21] Banyai L, Galbraith I, Ell C and Haug H 1987 *Phys. Rev.* B **36** 6099
[22] Herron N, Suna A and Wang Y 1992 *J. Chem. Soc., Dalton Trans.* 2329
[23] Mitzi D B, Feild C A, Schlesinger Z and Laibowitz R B 1995 *J. Solid State Chem.* **144** 159
    Voloshinovskii A S, Mikhailik V B, Myagkota S V, Ostrovskii I P and Pidzyrailo N S 1992 *Opt. Spectrosc.* **72** 486
[24] Bose S K, Satpathy S and Jepsen O 1993 *Phys. Rev.* B **47** 4276
[25] Dovesi R, Sanders V R and Roetti C 1992 *CRYSTAL 92 User Documentation* (Turin: University of Torino, Italy; Warrington: Daresbury Laboratory, UK)
[26] Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 284
[27] Palmer I J and Ladik J 1994 *J. Comput. Chem.* **15** 814
[28] Knop O, Wasylishen R E, White M A, Camerson B and Michiel J M 1990 *Can. J. Chem.* **68** 412
[29] Terzis A 19 unpublished