

# Electronic Structure of PbSe Nanowires

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## Abstract.

We present the tight binding calculations of the lead selenide nanowires: energy spectra of quantum confined states as a function of nanowire radius, dispersion in the full Brillouin zone, and the radial part of local electronic state density, which helps us to recognise valley splitting in the spectra. Also, we compare our results to *KP* perturbation theory predictions.

We show that the value of the valley splitting is comparable with the distance between two levels of size quantization and that it strongly depends on the arrangement of the atoms in the wire.

## 1. Introduction

The electronic structure of Lead Selenide nanocrystals (NC) was studied a lot by a variety of different methods, including *KP* perturbation theory, Density Functional Theory (DFT), and semi-empirical methods like a tight-binding or pseudopotential. However, there are few works dedicated to study intervalley energy splitting. In our work we will show that the contribution of an intervalley splitting is large and one can not ignore it in the calculations.

The revival of interest for these material is explained by the fact that wide range of nanostructures can be synthesized by modern chemistry methods. The study of quantum confinement effects opens an access to new industrial applications, despite the fact that PbSe is widely used material in optoelectronic devices such as lasers, detectors, etc. Strong quantum confinement effects allows for a wide range of operating wavelength  $[1 \div 5]\mu$ .

Unfortunately, the intervalley interaction is not well studied, it depends on NC symmetry, number of atomic layers, NC size, etc., and is strongly suppressed in structures with reduced symmetry [1]. To analyse how symmetry affect on the spectra we studied different types of wire. Since there is no exact theory that can describe the puzzling behaviour and predict the valley-mixing constant. To study the intervalley splitting in more details, we use a tight-binding (TB) calculations of the electronic structure of a PbSe nanowires.

## 2. Structure, and PbSe details

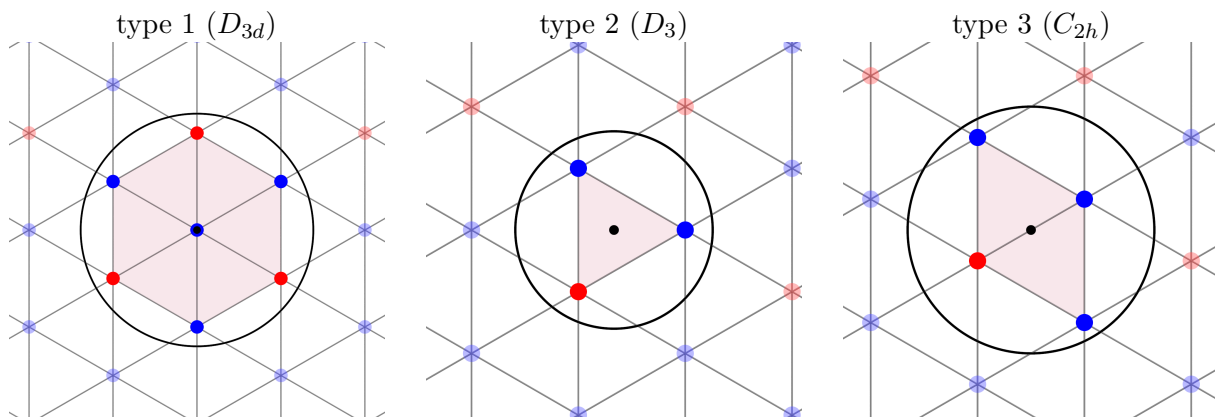
PbSe has the rocksalt crystal structure with the lattice constant about  $6.1\text{\AA}$ . The bulk crystal has the  $O_h^5$  symmetry group. It is a narrow direct band gap semiconductor ( $E_g \approx 0.28\text{eV}$  at  $300\text{K}$ ) with the band extrema at the  $L$  point of the Brillouine zone. Group of the wave vector at  $L$  point is  $D_{3d}$ . All lead chalcogenides have a similar bulk dispersion and lattice structure, in our study we consider only PbSe, but qualitatively the results are similar for other materials from this group.



In the work we study cylindrical wires. The point group of a periodical structure is defined by the point group of the elementary cell of the structure. We define the wire as an array of atoms which lay inside an ideal cylinder. The cylinder is determined by the radius, the axis direction and by the position of its center in the bulk semiconductor.

In general case of an arbitrary axis direction and the position of cylinder center, the resulting symmetry of the wire would be low. However, we are able to construct highly symmetric wires. We set the wire axis direction along the  $[111]$   $L$  valley. Then we consider three wire types with different microscopic structure. The first type is obtained by placing the center at an atom, the second is by placing the center between atoms and the third is by placing the center at the middle of a chemical bond, see Fig. 1. The surface of a wire, which is very close to a circle for large radius, is discretized on an atomic level. As a result, the arrangement of atoms at the wire surface is different and the microscopic symmetry will be different in three cases.

We notice that the position of the center does not always coincide with inversion center of a wire. Moreover, the second type of wire has no inversion center. This fact is really interesting since the lack of inversion may produce  $k$ -dependent spin-splitting, which we are able to calculate.



**Figure 1.** (Color online) Atomic arrangement for the three different types of wire. The red dots are Pb atoms, the blue ones are Se, solid circle is the border of an ideal cylinder, small black dot is the wire axis. The lattice in the figures is formed by three atomic planes (000), (111), (222) of the bulk crystal, as seen from  $[111]$  direction. Real atomistic structure within the ideal cylinder is highlighted.

The choice of the growth direction of the wire along the  $L$  valley leads to valley splitting of four equivalent  $L$  valleys in one longitudinal and three equivalent transverse due to mass anisotropy, which are quite easy to recognise. Because there are no irreducible representations in these groups with dimension greater than two, it is natural to expect further splitting of the valleys by the wire interfaces with expected degeneracy  $1 + 2 + 1$  for the ground state.

### 3. Details of the calculations

In our work we use the tight-binding method with the KP calculations for comparison.

#### 3.1. TB method

Tight-binding method is a widely used semi-empirical method. It gives good results in a reasonable computational time and it is quite simple to implement (compared to *ab initio* methods). We use this advantage to calculate the wires with a wide radius range.

The method is based on decomposition of the electron Schrödinger equation in the local basis of Löwdin molecular orbitals [2] – orthogonalized atomic-like orbitals. The Hamiltonian for

periodical structures in tight-binding method writes as:

$$H_{ml,m'l'}(\mathbf{k}) = \sum_j e^{i(\mathbf{R}_j + \mathbf{r}_l - \mathbf{r}_{l'}) \cdot \mathbf{k}} \langle \phi_{ml}(\mathbf{r} - \mathbf{r}_{jl}) | H | \phi_{m'l'}(\mathbf{r} - \mathbf{r}_{jl'}) \rangle, \quad (1)$$

where  $\mathbf{k}$  is the wavevector,  $m$  is the orbital index,  $j$  is the primitive cell index,  $l, l'$  are atom indexes,  $\phi_{ml}(\mathbf{r})$  is a Löwdin orbital.

To calculate the energy spectrum we have to solve an eigenproblem for a Hermitian sparse matrix of size  $[N_{atoms}N_{orbitals} \times N_{atoms}N_{orbitals}]$  at each  $k$  point of interest. Tight-binding approximation restrict the amount of neighbors in hamiltonian matrix with the coordination number (6 for cubic lattice) and the hamiltonian matrix takes a band form, hence computational difficulty is only about  $\mathcal{O}(N_{eigenvectors} \cdot N_{atoms} \cdot N_{orbitals})$ . For instance, elementary cell of 20 Å has about 500 atoms, and  $H_{tb}$  size is about  $[10000 \times 10000]$ .

For our work we use  $sp^3d^5s^*$  parametrization with spin-orbital interaction applied on  $p$  orbitals. Parameters were fitted [1] to accurately reproduce experimental effective masses at the  $L$  point and energies of special points in Brillouin Zone obtained in  $GW$  approximation. Then this set of TB parameters was also used in the KP approximation to compare two different approach.

### 3.2. KP method

This is the most popular method for calculating an energy spectra of nanocrystals. The method is in a reasonable agreement with experimental data for large NCs sizes. The main advantage of the method is the possibility to obtain the analytical solution in most cases.

All latest KP models describing PbSe [3, 4] are based on four-band envelop function model [5] with the following Hamiltonian for each  $L$  valley:

$$\hat{H}(\hat{\mathbf{p}}) = \begin{pmatrix} \left( \frac{E_g}{2} + \frac{\hat{p}_z^2}{2m_l^-} + \frac{\hat{p}_\perp^2}{2m_t^-} \right) \hat{U}_2 & \frac{P_t}{m_0} \hat{p}_z \hat{\sigma}_z + \frac{P_t}{m_0} (\hat{p}_\perp \hat{\sigma}_\perp) \\ \frac{P_t}{m_0} \hat{p}_z \hat{\sigma}_z + \frac{P_t}{m_0} (\hat{p}_\perp \hat{\sigma}_\perp) & - \left( \frac{E_g}{2} + \frac{\hat{p}_z^2}{2m_l^+} + \frac{\hat{p}_\perp^2}{2m_t^+} \right) \hat{U}_2 \end{pmatrix},$$

where  $\hat{U}_2$  is  $2 \times 2$  unit matrix,  $m_0$  is a free electron mass,  $\sigma$  are Pauli matrices, and  $P_{t(l)}$  is the transverse (longitudinal) momentum matrix component. KP parameters (momentum matrix, masses,  $E_g$ ) were fitted to the dispersion near  $L$  point (namely, its second and fourth derivatives) calculated in the TB approximation. Usually, the KP hamiltonian is solved in perturbation theory  $H = H_{symm} + H_{an}$ ,  $|H_{an}| \ll H_{symm}$  by first finding a quantum confined solutions of spherically symmetric part of the KP hamiltonian  $H_{symm}$  and treating anisotropic part as a perturbation. It was shown that the asymmetric part is significantly smaller than the main term [6, 4] for dots and wires, especially for ground states. Despite that wires have the cylindrical symmetry, but they can be considered with the spherically symmetric hamiltonian [3]. The spherically symmetric hamiltonian produces fourfold degenerated states for all types of wire. More advanced cylindrical KP model allows to estimate valley splitting with respect to a mass anisotropy [4].

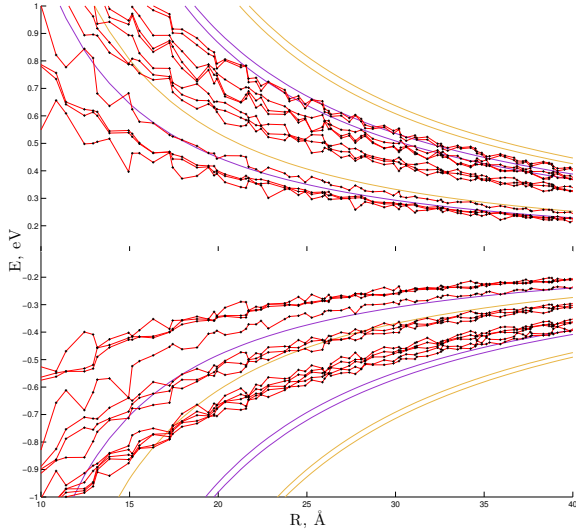
However, there is an additional intervalley splitting due to mixing at the interfaces, which can not be reproduced without significant modifications of KP model [1].

## 4. Results

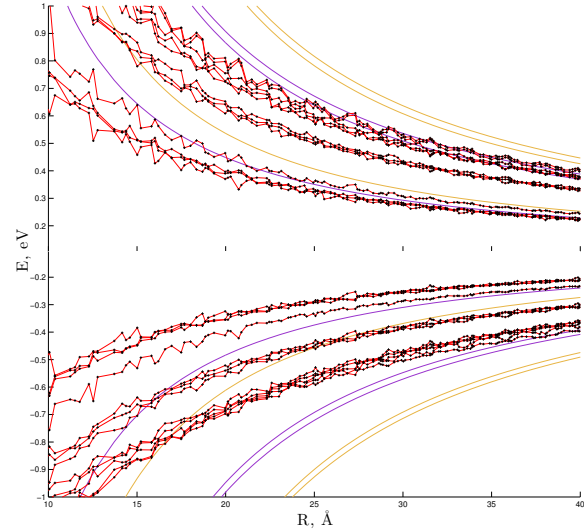
Below we present the results of tight-binding calculations: the dependence of the quantum confined levels on a wire radius compared with KP results, the spin splitting in the wires without spacial inversion center and the structure of local density of states for different quantum confined levels.

#### 4.1. Quantum confinement in the wires

One of the main result is a energy of quantum confined in the wires, calculated for different arrangement of atoms within the wires (1, 2, 3). We show only two of them, because the third type is very similar to the second. Tight-binding calculations are mapped on KP results with the same parameters. A thin line at the middle of the energy scale for both of those Figures 2, 3 shows  $\pm \frac{E_g}{2}$ , assuming zero energy corresponds to middle of the band gap.



**Figure 2.** (Color online) Energy of quantum confined states as a function of wire radius, the  $D_{3d}$  wire (“type 1”),



**Figure 3.** (Color online) Energy of quantum confined states as a function of wire radius, the  $D_3$  wire (“type 2”).

■ TB calculations, ■ KP singlet states, ■ KP triplet states

There are 12 first subbands in conduction and valence bands calculated at the  $L$  point of the one-dimensional Brillouin zone, defined as follows:

$$k_L = \mathbf{k}_L \cdot \mathbf{n}$$

All the states in the KP theory have two quantum number  $n, m$ . Wavefunctions of electrons localized in the wire is bessel functions  $J_m(r\lambda_n)$ , with the quantum number  $m$  corresponding to orbital momentum and  $n$  is the number of Bessel function roots in the interval  $(0, R]$ . Following [7, 3] there are three bulk subbands corresponded to  $\{m_{\frac{1}{2}}, n_1\}$  (ground state),  $\{m_{\frac{3}{2}}, n_1\}$  (first excited),  $\{m_{\frac{1}{2}}, n_2\}$  (second excited).

Fourfold degenerated bulk states are splitted by mass anisotropy into triplet and singlet, which can be clearly seen for the ground state energies in Figs. 2,3. For the first and second excited states there are no such obvious observations. Because of strong intervalley interaction these states can be shuffled. As a general rule, which has been explained in [1] for the quantum dots, there is strong symmetry-induced suppression of intervalley splitting in the wires of lower symmetry.

The analyzis of the valley splittings is hindered by the levels mixing and the fact that the value of valley splittings is compared with the distance between levels with different quantum numbers  $n, m$ . We were unable to find a simple criterion to extract KP quantum numbers from TB calculations, the only reliable approach is to analyze the spacial structure of the wavefunctions computed in TB method, see below.

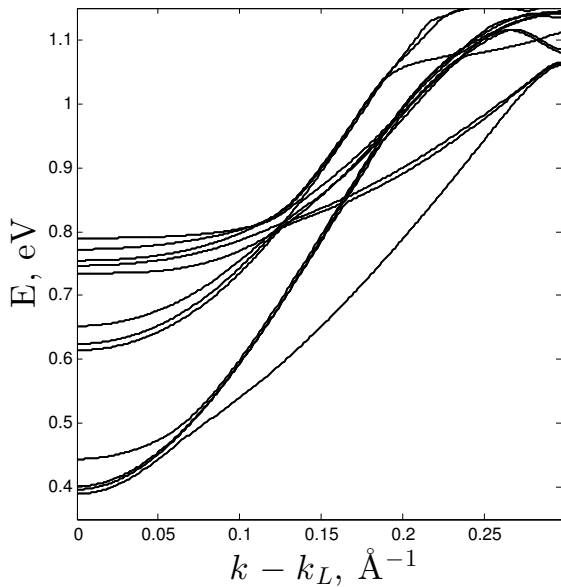
#### 4.2. Dispersion

Dispersion in the half-Brillouine zone, calculated in the TB method for 20Å wires is shown in the Figures 4, 5.

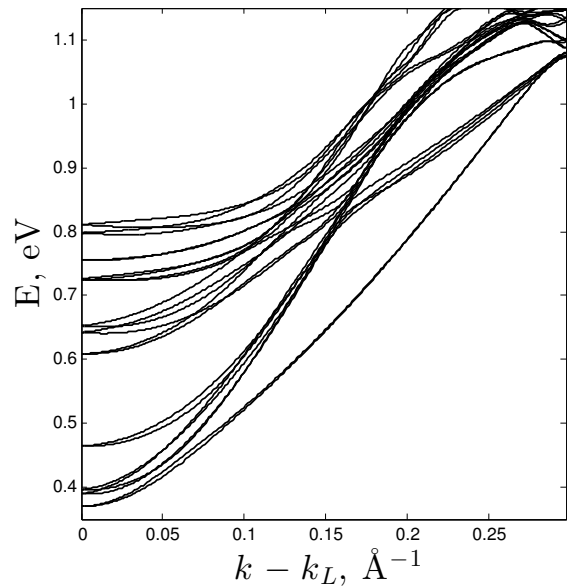
It is clear that for the ground states of the “type 1” wire effective masses can be calculated just as second derivative. However, the excited states are repulsed by k-dependent mixing and a special procedure should be used to remove all interaction effects. Another striking effect is that for the second wire type there is no Kramers degeneracy. It is well known that it may be lifted in the structures without inversion center. This effect is linear:

$$\Delta E_{spin} = \alpha(k - k_L), \quad (2)$$

with the spin-splitting constant  $\alpha(R)$  that is highly oscillating similar to intervalley splitting. Due to large spin-orbit interaction in PbSe (larger than the band gap in this material), the values of the spin splitting is also large.



**Figure 4.** Energy dispersion in the half-Brillouine zone in the 20Å wire of “type 1”,



**Figure 5.** Energy dispersion in the half-Brillouine zone in the 20Å wire of “type 2”.

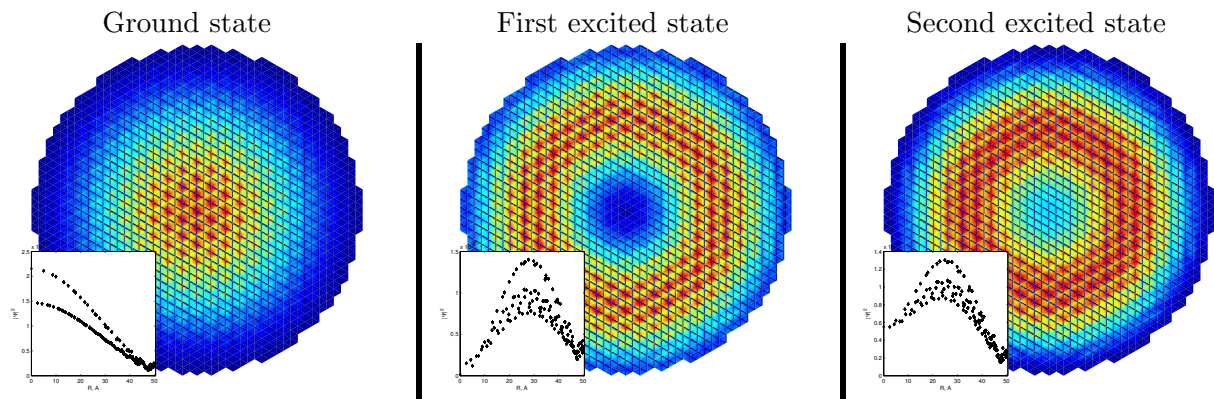
#### 4.3. Wavefunctions

To compare the states calculated in TB model with KP results, we used the analysis of local density of states (LDOS). Electron density (especially for big wire radiuses) is in a qualitative agreement with the density of confined states calculated in the KP approximation. It allows us to classify the states in accordance with their valley structure and quantum numbers. Electron density can be calculated as follows:

$$|\Psi(j)|^2 = \sum_l |V_c(j, l)|^2 + |V_a(j, l)|^2, \quad (3)$$

Where  $j$  is the atomic index in (111) plane (i.e. cartesian coordinates  $\{x, y\}$ ),  $l$  is orbital index,  $V_{c(a)}$  is an eigenvector value at a cation or an anion.

There is a qualitative difference between the first and the second excited states. The lowest momentum number  $m_{\frac{1}{2}}$  has a non-zero LDOS at the center of a wire, which allows us simply distinguish such states.



**Figure 6.** (Color online) LDOS of first three confined states in the 50Å wire of “type 1”.

## 5. Conclusion

Our TB calculations are in good agreement with KP theory for big wire radiuses, but the splitting of the valley triplet is the result of an surface-induced intervalley mixing and can't be predicted by a KP theory. The value of intervalley splitting is large which means that KP theory may not be used for the quantitative analysis of electron states in PbSe wires.

The effect of an intervalley splitting on excited states is even more pronounced than for the ground level as the order of the levels is changed in comparison with KP predictions. We stress that this effect is important for the analysis of optical spectra in such structures: as shown in [8], optical transitions from a ground valence to excited conduction states are about 30% of transitions between ground states.

Also, we show that in the wires without spacial inversion the linear spin splitting may be observed and its value is giant in comparison with other semiconductors.

## References

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