

# On the computer simulations of electron states of ionic nanosystems with extended defects

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**Abstract.** The electron states of nanosystems of ionic compounds AgCl and KCl with extended defects (charged defects, edge dislocations) were under consideration. The semi-empirical tight-binding approximation and different calculation methods were used. The obtained results and efficiency of calculation schemes are discussed. This work is an improvement of our early investigations.

## 1. Introduction

The notion of the “extended defect” means a defect which perturbs extensive region of a crystal. Dislocations and charged defects in ionic systems are extended defects as a rule. The calculation procedures for equilibrium space configurations and electron states of such defects in polar semiconductors and insulators have some particularities caused by long range Coulomb interaction and effects of polarization. Which is why the executions of self-consistent calculations of electron structure of polar systems with extended defects cause serious difficulties. But in special case of polar systems which consist of the “whole ions” it’s possible to use the partial self-consistency approximation [1]. Some applications of computational approaches in partial self-consistency approximation are been considered in present paper.

## 2. Models and methods

Semi-empirical techniques was used. At the first step the equilibrium geometry structure of nanocrystal (NC) was calculated within the model of pointlike polarizable ions by minimization of the total potential energy over the ion coordinates or by molecular dynamics method. Next, after determining of the ions coordinates in the equilibrium NC configuration the electron structure was calculated by semi-empirical self-consistent tight-binding method. If NC had large size and contained “whole ions” only, the partial self-consistency approximation was used. The use of partial self-consistency allow us to apply the effective methods without executing of unitary transformation of Hamiltonian matrixes. For example, numerical investigations of size effect influence on electronic structure of KCl nanocrystal (NC) with charged surface defect were carried out with the use of such algorithms, during which maximal NC under consideration was  $(K_{7504}Cl_{7505})^-$ . For more details, see the papers [1, 2]. Naturally, for NC with some hundred ions the standard problems of calculations of eigenvalues and eigenvectors are resolved quite efficiently.

In this work we have restricted the study of extended defects by charged defects only. Namely, adsorbed ion  $Ag^+$  on surface of NC  $AgCl$  has been considered. This problem was studied by



us earlier [2]. In present paper the additional results of computer simulation of the localized electron states and the probabilities of quantum transitions are presented.

Generally speaking, absorbed energy is not equal to a difference of one-particle energies of system in the ground state. However, with a view of the qualitative analysis it is assumed very often [3, 4]. According to these papers, in the present work the simple formulas for calculations of probabilities of transitions and absorption factor in the electric dipole approximation (see, for example, [5]) were used:

$$\mathcal{P}_{n \rightarrow n'} = c_1 |\mathbf{e} \cdot \mathbf{M}_{n'n}|^2 \delta(E_{n'} - E_n - \hbar\omega), \quad (1)$$

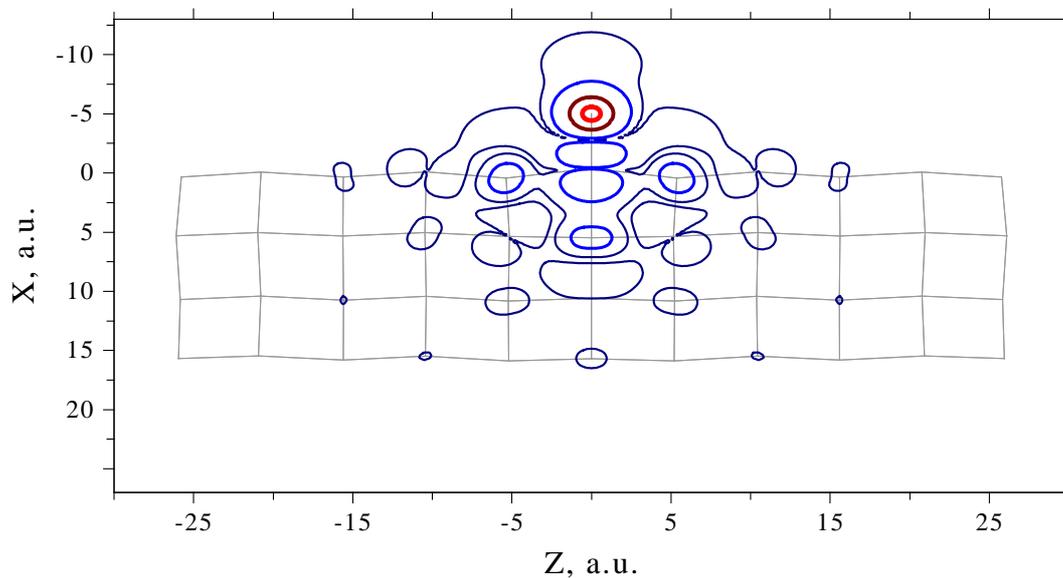
$$\alpha(\hbar\omega) = \frac{c_2}{\hbar\omega} \sum_{n,n'} |\mathbf{e} \cdot \mathbf{M}_{n'n}|^2 \delta(E_{n'} - E_n - \hbar\omega), \quad (2)$$

where

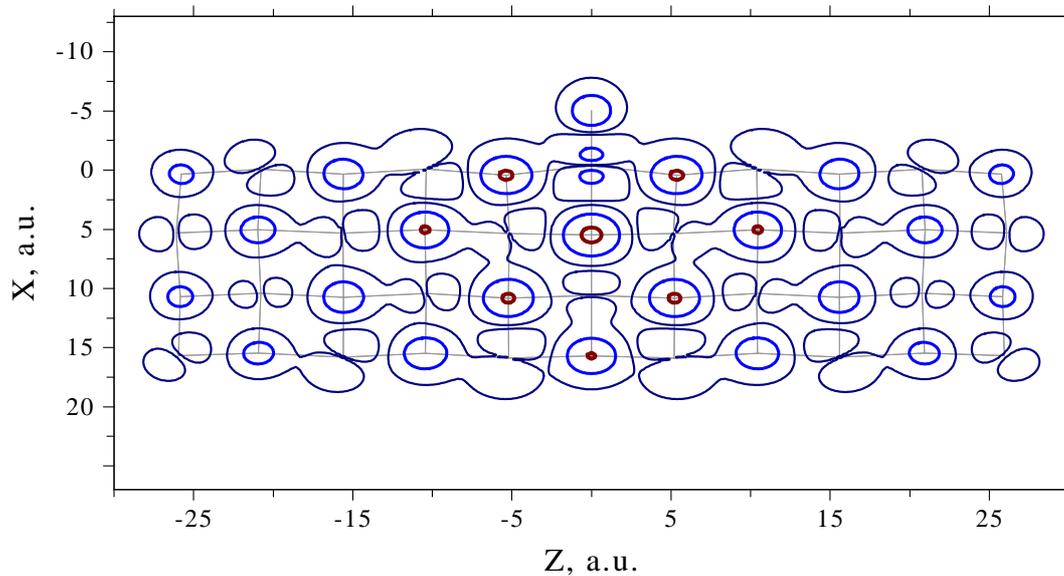
$$\mathbf{e} \cdot \mathbf{M}_{n'n} = \langle \psi_{n'} | -i\hbar \mathbf{e} \cdot \nabla | \psi_n \rangle. \quad (3)$$

Here (3) – matrix element of optical transition;  $c_1, c_2$  – constants;  $\mathbf{e}$  – unit vector in direction of an electric field strength;  $E_n$  and  $\psi_n$  – energy and a wave function  $n$  th one-electron state;  $\hbar\omega$  – energy of quantum.

Following the paper [4], the atomic orbitals (AOs), usually applied in non-empirical quantum chemistry, were used for calculation of matrix elements (3). Such procedure has allowed authors of paper [4] to carry out the successful analysis of dipole matrix elements for the silicon quantum wires in the qualitative agreement with later non-empirical DFT calculations. Further, AOs, generally speaking, do not form orthonormal basis set of functions. Meanwhile, in our variant of tight-binding method it is supposed. Therefore the orthogonalization and normalization of AOs were carry out with use of iterative algorithm [6].



**Figure 1.** Module of the wave function of AgCl NC with the adsorbed silver ion (485 ions): first unoccupied state.



**Figure 2.** Module of the wave function of AgCl NC with the adsorbed silver ion (485 ions): second unoccupied state.

### 3. Results

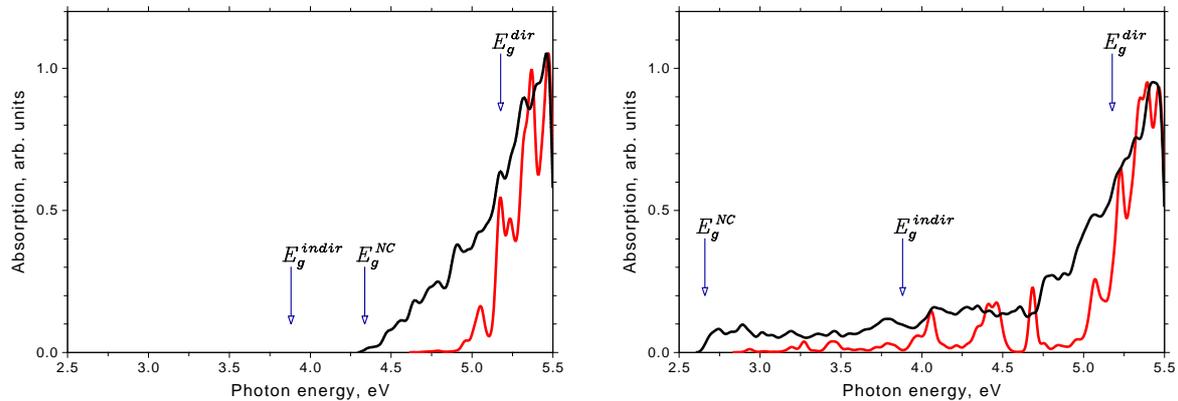
The investigated nanocrystals contained four layers  $11 \times 11$  ions without (484 ions – neutral system) and with adsorbed ion  $Ag^+$  (485 ion – charged system); see fig. 2a, [2]. The linear combinations of Gauss Cartesian functions as the basis orbitals with parameters taken from [7] for 4d and 5s shells of silver and from the tables [8] for 3p shell of chlorine were used.

There is strong localization of first unoccupied state near adsorbed ion, see fig. 1. For comparison the module of a wave function for the second unoccupied state is given, fig. 2. The contours of the wave functions are presented in XZ plane (adsorbed ion's position on vertical axis). The function values that define the contour lines to be calculated are 0.5 (red color), 0.1 (dark-red color), 0.01 (blue color), and 0.001 (dark-blue color).

How much strongly the influences of adsorbed ion on the nanocrystal absorption spectrum? The calculated absorption spectrums and joint density of states are presented on fig. 3. In the formula (2)  $|\mathbf{e} \cdot \mathbf{M}_{n'n}|^2$  it has been exchanged on  $|\mathbf{e}_x \cdot \mathbf{M}_{n'n}|^2 + |\mathbf{e}_y \cdot \mathbf{M}_{n'n}|^2 + |\mathbf{e}_z \cdot \mathbf{M}_{n'n}|^2$ .

The peak value of probability of quantum transition for NC  $Ag_{242}Cl_{242}$  at 5.5 eV was accepted equal to unity. Further this normalization was taken into account for plotting of other spectrums. Joint densities of states were calculated with use of formula (2) in which the matrix element of optical transition was equal to unity. According to the practice of calculation of such expressions, the Dirac delta function in the formula (2) was exchanged by a Gaussian. For the best visual perception the joint densities of states were normed so that their maximums coincided with maximums of corresponding absorption spectrums.

The labels  $E_g^{indir}$  (the indirect forbidden gap),  $E_g^{NC}$  (the difference between lowest unoccupied and highest occupied energy levels of NC), and  $E_g^{dir}$  (the direct forbidden gap) are presented in fig 3 also. It is necessary to note, that the direct forbidden gap was found by the calculations of joint density of states for ideal crystal.



**Figure 3.** The absorption spectrums (red lines) and joint densities of states for NC  $Ag_{242}Cl_{242}$  (left) and  $(Ag_{243}Cl_{242})^+$  (right).

#### 4. Conclusions

The absorption spectrum and joint density of states are essentially different near the absorption edge of NC  $Ag_{242}Cl_{242}$  (fig. 3, left). The left boundary of joint density of states corresponds to energy gap of NC (energy gap is equal to difference of energy of the lowest unoccupied level and energy of the uppermost occupied level). Meanwhile, appreciable absorption begins with energies which are about the width of direct forbidden gap of ideal crystal  $AgCl$ !

Thus, in the present work with use of computer simulation it is shown: 1) presence of the short-range order in silver chloride NC consisting of several hundreds of ions is affected on a absorption spectrum: absorption spectrum of NC is similar to an absorption spectrum of an ideal crystal  $AgCl$  near to its edge; 2) extended charge defect leads to appearance of absorption below edge of absorption spectrum of an ideal crystal  $AgCl$ .

#### References

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