The use of semiempirical algorithms for electronic levels calculations of polar nanosystems with the partial self-consistency

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Abstract. Three semiempirical algorithms for electronic levels calculations of polar nanosystems with the partial self-consistency are discussed. These algorithms are based on the model of pointlike polarized ions and on the self-consistent modification of semiempirical tight-binding theory of Slater and Koster. The basic feature of this work is the use of partial self-consistency which allows to simplify a mathematical formalism and to accelerate considerably the process of the calculations for nanosystems containing “whole ions”. The obtained results for such systems, as was shown, are in rather good qualitative agreement with the results of non-empirical calculations. The presented algorithms can be effectively used for calculations of the electronic structure of polar nanosystems containing $\sim 10^4$ and more ions.

1. Introduction

To do the extended defects modelling (dislocations, charged defects) in nanocrystals (NC) there is a need to consider the systems containing $\sim 10^4$ and more atoms or ions. Over the last two decades the progress in computer technics and the accessibility of sophisticated special-purpose computer programs (which, as a rule, were being made by scientific groups with high qualification) for researchers allowed to do the self-consistent non-empirical calculations of electron structure of crystals with defects and nanosystems on a mass scale. Basically, these calculations are being executed in the framework of the density functional theory. Also much success was achieved in a development of the calculation procedures. Now it is possible, for example, the calculations of electronic states of huge systems with using of linear-scaled methods [1]. Let’s note, that such computing procedures become rather effective only with the use of powerful multiprocessing computing systems. Not all of researchers have a possibility to use such systems, and the use of such systems is unjustified in all cases. Therefore when solving the problems with pretension to reasonable qualitative results are a topical problem of using the semiempirical approaches which would be applicable to calculations on the modern personal computers. It seems to the author the development of such semiempirical techniques is a topical problem.

2. Models and methods

As is known, when doing traditional calculations of electronic structure of polyatomic systems within the limits of a tight-binding method it is necessary to calculate the eigenvalues and the
eigenvectors of a Hamiltonian matrix. In the present work the alternative approaches based on absolutely other mathematical formalism are offered. Most correctly suggested approaches are applicable to a special case of polar systems which consist of the “whole ions”. We will discuss such systems further.

In the present work our attention is focused on consideration of the electronic structure algorithms for binary polar nanocrystals such as AgCl and KCl for example. The equilibrium positions of ions in these systems were calculated within the model of pointlike polarized ions by the minimization of the total potential energy over the ion coordinates by Fletcher–Reeves [2] method and by method of molecular dynamics. Each of the ions in the considered model is regarded as a point quasi-elastic dipole. For each step of the search for the equilibrium space ions configuration their dipole moments were being found in a self-consistent way. Next, after determining of the ions coordinates in the equilibrium NC configuration the electron structure was calculated by self-consistent tight-binding method (SCTBM) with orthogonal basis set. See details in paper [3].

The new point in our calculation technics is the use of partial self-consistency for calculations of electron states of nanosystems consisting of “whole ions”. Within the limits of this scheme the electrical dipole moments of ions, which were obtained in model of pointlike polarized ions, were used for evaluation of corrections for diagonal elements of Hamiltonian matrix; effective charges are thus determined by input data. In this approach the iterated self-consistent calculations are not being executed! Clearly, that such approach can be correct only for systems in which there is no essential reallocation of charge density, e.g. for systems with whole ions.

The use of partial self-consistency allow us to apply the effective methods without executing of unitary transformation of Hamiltonian matrixes. It is evident that such unitary transformations are the hot-spots in computer codes.

About the first algorithm. After the evaluation of a matrix of a Hamiltonian we do not solve the task about eigenvalues, but we use the known theorem ([4], p. 204) which can be formulated as follows. Let us suppose that we calculated the Hamiltonian matrix which is the real symmetric matrix. For the arbitrary scalar \( \lambda \) we organise a matrix \( ||H|| - \lambda ||I|| \) and further will fulfil a triangular factorization

\[
||H|| - \lambda ||I|| = ||U||^T ||D|| ||U||,
\]

(1)

where \( ||I|| \) is unit matrix, \( ||U|| \) is upper triangular with unit diagonal, \( ||D|| \) is diagonal matrix. Then, the number of eigenvalues less than \( \lambda \) is equal to the number of negative elements of the diagonal matrix \( ||D|| \). If we will change \( \lambda \) with the given step, will do on each step a triangular factorization (1) and will calculate the number of the negative diagonal elements of matrix \( ||D|| \), then it will be easy to draw the histogram of total density of states.

Further, separate eigenvalue of \( ||H|| \) can be localised by the bisection method. It is convenient to use such approach for studying the local levels of localized states of nanocrystal. As usual the matrix of a Hamiltonian for nanocrystal in the framework of semiempirical tight-binding method is sparse real symmetric matrix. Naturally, the efficiency of a computer code rises sharply if we use algorithms to sparse matrix.

About the second algorithm. It is a well-known algorithm of simultaneous iteration of eigenvectors ([5], p.284) for the evaluation of energy level and corresponding orbital coefficients. Certainly, this method is applied to a matrix \( (||H|| - \lambda ||I||)^{-1} \), where \( \lambda \) has value in some energy interval (in zero approximation). In case of the sparse matrixes efficiency increases if we calculate the vector \( (||H|| - \lambda ||I||)^{-1} x \) by solving the equation \( (||H|| - \lambda ||I||) y = x \). This algorithm was applied, for example, for calculations of electronic levels of KCl nanocrystal which consisted of \( > 15000 \) ions.

About the third algorithm. The recursion method works excellently in partial self-consistency approximation. The recursion method in variant of Nex was used [6, 7].
Figure 1. The isolated asperities on surface of $KCl$ nanocrystal (657 ions); a) negatively charged surface defect ($K_{4}Cl_{5}^{-}$); b) positively charged surface defect ($K_{5}Cl_{4}^{+}$). Black disk – cation.

Table 1. Nanocrystal $KCl$ in form of $n \times n \times (n - 1) + 3 \times 3$ ions with negatively charged surface defect: some characteristic energies (eV).

|                  | $n/N_{AO}$ | $E_{min}$ | $E_{HONO}$ | $E_{LUNO}$ | $E_{max}$ |
|------------------|------------|-----------|-------------|-------------|-----------|
| $(K_{328}Cl_{329})^{-}$ | 9/1315     | -8.698    | -7.218      | 1.100       | 3.982     |
| $(K_{1579}Cl_{1580})^{-}$ | 15/6319    | -9.018    | -7.500      | 0.624       | 3.690     |
| $(K_{4414}Cl_{4415})^{-}$ | 21/17659   | -9.161    | -7.615      | 0.433       | 3.567     |
| $(K_{7504}Cl_{7505})^{-}$ | 25/30019   | -9.220    | -7.661      | 0.400       | 3.519     |
| extrapolation     | $\infty/\infty$ | -9.537    | -7.891      | 0.135       | 3.268     |
| crystal $KCl$     | -          | -9.466    | -8.690      | 0.000       | 2.972     |

3. Results
These three algorithms were used for theoretical investigations of electronic structure of $AgCl$ and $KCl$ nanosystems with atomically rough surfaces, edge dislocations, and isoelectronic substitutional impurities [3, 8–12]. For example numerical investigations of size effect influence on electronic structure of $KCl$ nanocrystal with charged surface defect were carried out with the use of the algorithms discussed above [12]. The charged defects in the form of isolated surface asperity with size of $3 \times 3$ ions and located on one of surfaces of electrically neutral nanocrystals $KCl$ have been investigated. The isolated surface asperity represents the charged defect – either $(K_{5}Cl_{4})^{+}$, or $(K_{4}Cl_{5})^{-}$. These surface defects are shown on fig. 1. The nanocrystals without the charged defects had form of parallelepipeds in the size $n \times n \times (n - 1)$, $n = 9, 15, 21, 25$. Thus, studied nanocrystals with the charged defects contained 657, 3159, 8829 and 15009 ions.
accordingly. Some numerical results can be seen in table 1. Here $E_{\text{min}}$ and $E_{\text{max}}$ are the energies of lowest and highest levels; $N_{\text{AO}}$ is number of basic atomic functions.

An alternative calculation of electronic energy spectrum of nanocrystals is of great interest. The non-empirical calculations of some small nanocrystals $\text{AgCl}$ and $\text{KCl}$ were carried out in the framework of the density functional theory and in Hartree-Fock-Rutaa approximation with the use of pseudopotentials. It was found that the results of non-empirical calculations are in reasonably good agreement with the results of our semiempirical calculations.

Non-empirical quantum-chemical calculations were made with the use of the program “Gaussian 03” [13] which was installed on the parallel computer cluster of the Digital Technologies Department of Computer Sciences Faculty, Voronezh State University, and with the use of the program “Firefly” [14, 15] on the supercomputer “Chebyshev” of Moscow State University.

4. Conclusions
To summarize briefly, the partial self-consistency approximation allows to use very effective algorithms for the calculation of electron structure of polar nanocrystals consisting of “whole ions”. The obtained results are qualitatively reasonable.

Acknowledgments
Many thanks to Professor S. D. Kurgalin (Head of the Digital Technologies Department of Voronezh State University) for the possibility of using the computer cluster.

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