

# QUANTUM THEORETICAL MODELLING OF HgS, HgSe, PbS, PbSe, Ag<sub>2</sub>S AND Ag<sub>2</sub>Se THIN FILMS BY THE FINITE-CLUSTER METHODOLOGY. COMPARISON WITH THE EXPERIMENTAL RESULTS

Metodija Najdoski, Biljana Pejova, Ivan Grozdanov and Ljupco Pejov

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University, POB 162, Arhimedova 5, 91000 Skopje, Republic of Macedonia,  
e-mail: metonajd@iunona.pmf.ukim.edu.mk

**Abstract.** A quantum theoretical study of several semi-conducting metal sulfide and metal selenide thin films was performed employing the finite cluster methodology. All of the calculations were based on fully non-empirical Hamiltonians. Both conventional Hartree-Fock as well as Density Functional approaches were implemented. The Hartree-Fock or the Kohn-Sham equations were solved within the LANL2DZ basis set (D95 on the first row elements, Los Alamos ECP plus DZ on Na-Bi). In order to account for the relativistic effects, the inner shell electrons of the heavy atoms were modeled using effective core potentials, implemented in the mentioned basis. Both the effect of inclusion of the electron correlation and tying off the dangling orbitals of Hg, Pb and Ag atoms on the calculated properties of the mentioned semiconductors were discussed. The calculated optical and electrical parameters were compared to the experimental ones for films fabricated by chemical bath technique.

**Key words:** metal chalcogenides, thin solid films, finite-cluster methodology, non-empirical Hamiltonian, semiconductors.

## 1. Introduction

It has been long recognized that surfaces and interfaces play an important role in determining the electronic properties of solid-state devices. Thus, the extremely fast development of the silicon-based technology is mostly due to the nearly perfect Si-SiO<sub>2</sub> interface [1]. However, the selenium-based materials are increasing in popularity, due to their attractive electronic properties [2-7]. This especially refers to metal selenide (as well as to metal sulfide) thin films. By controlling the size of crystals forming the thin film (adjusting the experimental conditions for the film deposition), it is possible to control various opto-electronic properties of these materials, such as the bandgap energy, absorption edge, etc. This is mainly due to the size-quantization effects for the nanocrystalline thin films [8].

We have recently published several chemical bath deposition methods for fabrication of metal sulfide and metal selenide thin films [2-7]. Most of the films are characterized with very interesting optical and electrical properties. Thus, both mercury(II) selenide and silver selenide films obtained by chemical bath deposition methodology exhibit strong {111} texturing and pronounced quantum size effects, which reflect in their optical and electrical properties. These films are potentially applicable in various opto-electronic devices, such as energy-conserving cells.

Generally speaking, the problem for theoretical prediction of a given property of these quasi-two dimensional systems is of great technological and fundamental importance. Many theoretical approaches have been proposed that allow derivation of analytical expressions that connect the value of a given parameter referring to nanocrystals with the bulk value. However, all of these approaches are more or less phenomenological. It is therefore of significant valuability to establish an exact (*ab initio*) approach that would allow efficient and low cost procedure for calculations of various opto-electronic parameters of the mentioned systems.

In the present work, we report a fully non-empirical study of several metal chalcogenide thin films, applying the finite cluster methodology.

## 2. Theoretical and computational details

The finite-cluster methodology is a very efficient alternative to the exact full *ab initio* treatment of periodic systems [1]. First, the relatively low computational cost of this methodology allows its applicability to a wide variety of systems. Further, it is possible to account for the long-range interactions and to overcome the size truncation by tying off the dangling orbitals of particular atoms in the structure.

Atomic clusters consisting of six formula units (for HgS, HgSe, PbS and PbSe) and 3 formula units (for the Ag<sub>2</sub>S and Ag<sub>2</sub>Se) were used in the calculations.

In the present study, we have applied the Hartree-Fock-Roothaan Self-Consistent-Field molecular orbital method (HFR-SCF-MO) [9, 10]. In order to at least partially account for the relativistic effects (that are of certain importance for these systems), the inner electrons of the atoms within the cluster were represented by effective core potentials. On the other hand, basis sets consisting of contracted gaussian-type functions (GTFs) were chosen to represent the valence electrons. In all of the calculations, the LANL2DZ basis set was adopted for the orbital expansion. This basis is, in fact, D95 on first row elements [11], Los Alamos ECP plus DZ on Na-Bi [12-14], and, as mentioned, contains an effective core potential representation of the inner electrons. The direct SCF procedure was used in all of the calculations (the two-electron integrals were recomputed in each iteration).

All calculations were performed with the Gaussian94w series of programs [15].

## 3. Results and Discussion

The calculated energy spectra of the studied (AB)<sub>6</sub> or (A<sub>2</sub>B)<sub>3</sub> clusters at HFR-SCF-MO/LANL2DZ level of theory are presented in Table 1. The reminiscent of the band structures are obvious. Note that not all of the states are presented in table 1, but only those which are substantial in interpreting the properties of interest.

The calculated HOMO-LUMO energy differences for the studied clusters on the basis of the HFR-SCF/LANL2DZ method are presented in Table 2, together with the experimentally measured band gap energies on the basis of the optical absorption data. Although the HOMO-LUMO energetic difference is not straightforwardly comparable to the measured band gap energy, it can serve as a very useful parameter, especially for the prediction of trends in a series of structurally similar materials. Note that, in fact, the measured band gap energy is not an intrinsic property of a given type of (intrinsic) semiconductor, but is a crystal-size dependent quantity, due to the size quantization effects. However, having in mind that the experimental values refer predominantly to nanocrystalline materials, and that the employed level of theory is not very high, the presented results are encouraging. Inclusion of dynamical electron correlation effects as well as an exact inclusion of the core electron representation via more flexible basis (instead of the effective core potential representation) would improve the results significantly. However, the Density functional level of theory (the gradient corrected variant) is very slow to converge, and often a large number of cycles within an SCF procedure is required to achieve self-consistence, thus enlarging the computational costs significantly.

Table 1. The HFR-SCF-MO/LANL2DZ energy spectra of the studied electroneutral (AB)<sub>6</sub> or (A<sub>2</sub>B)<sub>3</sub> clusters (*E* / atomic units); virtual states are denoted by a superscript "v"

PbS	PbSe	HgS	HgSe	Ag <sub>2</sub> Se
- 2.20263	-2.34868	-2.52355	-2.57299	-5.05776
-1.84593	-1.93384	...	...	...
-1.76601	-1.80154	-1.24492	-1.25621	-1.03199
-1.62478	-1.68821	-1.20401	-1.21977	-0.96203
-1.47586	-1.50404	-1.16966	-1.21806	-0.95426
-1.33986	-1.38251	-1.14961	-1.20796	-0.93999
-1.30212	-1.32030	-1.04387	-1.13820	-0.91107
-1.15192	-1.18815	-1.00734	-1.05749	-0.88425
-1.11956	-1.10388	-0.97020	-1.02207	-0.88020
-1.11688	-1.07267	-0.94485	-1.02138	-0.85910
-0.94348	-0.95563	-0.88170	-0.90940	-0.84843
-0.89911	-0.91322	-0.86397	-0.88594	-0.83336
-0.89784	-0.89479	-0.85050	-0.88456	-0.82223
-0.83755	-0.79519	-0.83435	-0.83910	-0.77301
-0.77777	-0.76298	-0.69951	-0.68443	-0.75718

-0.73789	-0.73157	-0.69331	-0.67387	-0.74646
-0.70644	-0.72893	-0.63875	-0.66761	-0.72343
-0.65020	-0.63189	-0.60472	-0.61140	-0.71418
-0.64072	-0.60964	-0.60036	-0.57965	-0.68034
-0.63201	-0.59760	-0.51003	-0.52701	-0.64214
-0.49756	-0.44125	-0.46718	-0.51493	-0.63807
-0.45436	-0.41870	-0.45808	-0.45148	-0.59223
-0.41882	-0.38315	-0.45127	-0.44911	-0.48559
-0.37514	-0.35116	-0.43351	-0.38634	-0.44797
-0.35118	-0.31990	-0.39311	-0.38031	-0.43636
-0.32931	-0.31108	-0.28275	-0.28472	-0.40063
-0.30516	-0.29622	-0.25561	-0.23382	-0.36551
-0.29301	-0.25659	-0.23937	-0.21434	-0.32270
-0.24818	-0.24000	-0.20810	-0.21244	-0.25159
-0.16179	-0.20752	-0.18543	-0.16748	-0.19255
-0.04724 <sup>v</sup>	0.02745 <sup>v</sup>	0.00824 <sup>v</sup>	0.02015 <sup>v</sup>	0.01299 <sup>v</sup>
0.00282 <sup>v</sup>	0.03331 <sup>v</sup>	0.01604 <sup>v</sup>	0.02282 <sup>v</sup>	0.02672 <sup>v</sup>
0.04025 <sup>v</sup>	0.04541 <sup>v</sup>	0.04111 <sup>v</sup>	0.04197 <sup>v</sup>	0.02803 <sup>v</sup>
0.04278 <sup>v</sup>	0.06782 <sup>v</sup>	0.04347 <sup>v</sup>	0.05093 <sup>v</sup>	0.03287 <sup>v</sup>

Our further efforts will be directed towards the description of the quantum size effects for finite systems via a fully *ab initio* Hamiltonian. Also, a reformulation of the density functional algorithms in a way analogous to the HPHF method would probably lead to a significant reduction of the computational cost.

Table 1. The HFR-SCF-MO/LANL2DZ HOMO-LUMO energy differences of the studied electroneutral (AB)<sub>6</sub> or (A<sub>2</sub>B)<sub>3</sub> clusters together with the experimentally determined band gap energies on the basis of the optical absorption data

	PbS	PbSe	HgS	HgSe	Ag <sub>2</sub> Se
$\Delta E$ (HOMO-LUMO)/eV	3.12	6.39	5.27	5.11	5.59
$E_g$ (experimental)/eV	-	-	3.10	2.50	1.70

**Апстракт.** Изведена е квантно теориска студија на неколку полупроводнички метал сулфидни и метал селенидни тенки филмови со методот на конечни кластери. Сите пресметки се базирани на потполно неемпириски Хамилтонијани. Имплементиран е стандардниот пристап на Hartri-Fok, како и оние базирани на теоријата на функционал на густината. Hartri-Fokovite или Кон-Шемовите равенки се решени во рамките на LANL2DZ базисниот сет (D95 на елементите од првата периода, и Los Alamos ECP plus DZ за серијата Na-Bi). За да се вклучат релативистичките ефекти, внатрешните електрони на тешките атоми се моделирани ползувајќи ефективни потенцијали, имплементирани во споменатиот базисен сет. Дискутирани се ефектите на вфиксирањег на слободните орбитали на Hg, Pb i Ag атомите. Теориски добиените параметри се споредени со експерименталните за филмови добиени со методот на хемиска депозиција.

#### 4. References

- [1] S. Gayen, W. C. Ermler, C. J. Sandroff, J. Chem. Phys., 94 (1991) 729.
- [2] B. Pejova, M. Najdoski, I. Grozdanov, S. K. Dey, J. Mater. Chem. (in press).
- [3] M. Najdoski, I. Grozdanov, S. K. Dey, B. Siracevska, J. Mater. Chem., 8 (1998) 2213.
- [4] B. Pejova, M. Najdoski, I. Grozdanov, S. K. Dey, Mater. Lett. (submitted).
- [5] I. Grozdanov, M. Najdoski, S. K. Dey, Mater. Lett., 38 (1999) 28.
- [6] I. Grozdanov, Appl. Surf. Sci., 84 (1995) 325.
- [7] M. Najdoski, B. Pejova, I. Grozdanov, S. K. Dey, (to be submitted).
- [8] S. Gorer, G. Hodes, J. Phys. Chem., 98 (1994) 5338.
- [9] C. C. J. Roothaan, Rev. Mod. Phys., 23 (1951) 69.

- [10] C. C. J. Roothaan, *Rev. Mod. Phys.*, 32 (1960) 179.
- [11] T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer, III, Plenum: New York, 1976, 1-28.
- [12] P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 82 (1985) 270.
- [13] W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 82 (1985) 284.
- [14] P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 82 (1985) 299.
- [15] Gaussian 94 (Revision B.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995..