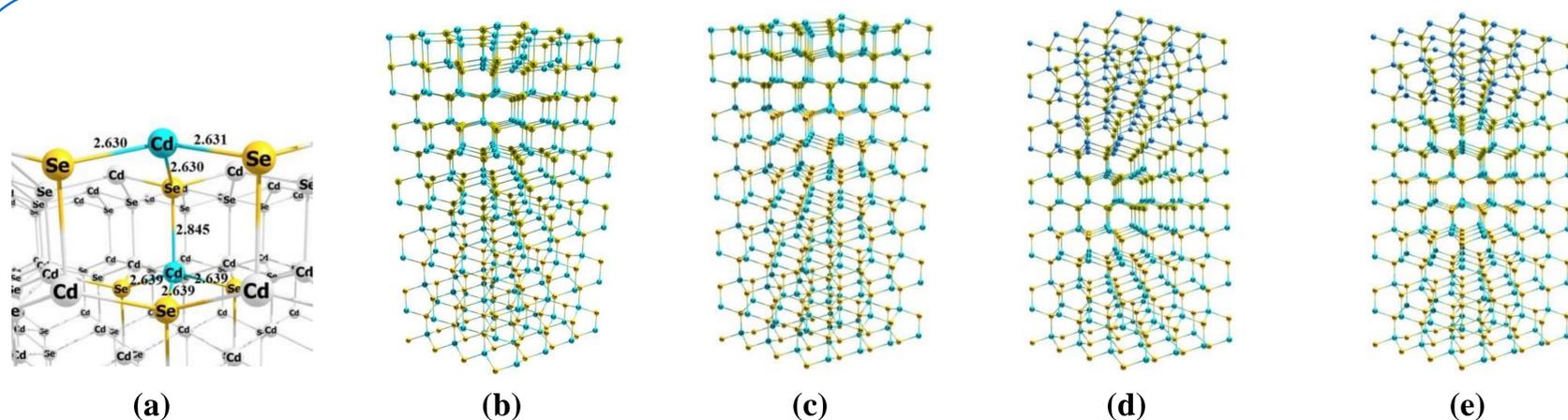


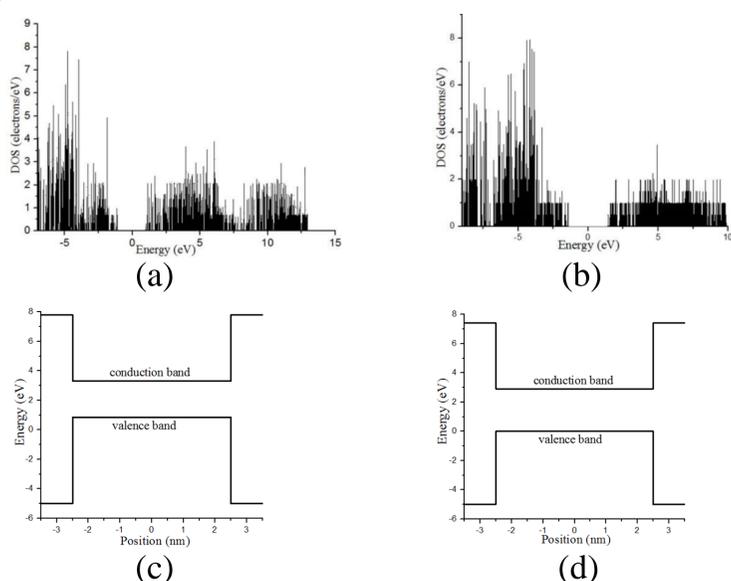
Quantum dots (QDs) are one of the well-known semiconductor nanoparticles due to their remarkable luminescence efficiency, controlled by the size and shape of particles, emission in a wide spectrum range, good photostability and fairly long lifetimes of the excited states. In recent years the opportunities of their practical application were significantly expanded: lasers, solar cells, displays, quantum computing technologies, photovoltaic, bioimaging, LEDs, transistors, etc. Quantum-chemical study of these objects not only provides experimentally unobtainable data but also allows to predict their physicochemical behavior prior to synthesis, purposefully vary their properties and design devices with custom-oriented behavior.

In this work the Hubbard corrected density functional theory was applied for the quantum-chemical simulation of the structural and electronic properties of CdSe/CdS core/shell and CdSe/CdS/ZnS core/shell/shell QDs with hexagonal structure and different number of monolayers in the core and the shell. It was shown that accurate prediction of their different properties might require different Hubbard parameters. The simulation results revealed insignificant difference of quantum dots core structure from the crystalline structure of bulk materials. Optimization of their surface geometry revealed a deviation of the surface structural parameters from the internal structure. The influence of the shell nature and thickness on the geometric characteristics and optoelectronic properties of quantum dots was studied. The band alignment was found to be type I with shells that play the role of the energy barrier in the processes of hole and surface electron trapping.



Optimized geometries of CdSe surface (a), CdSe/CdS with 3/7 (b) and 7/3 monolayers ratio (c), CdSe/CdS/ZnS with 3/2/5 (d) and 5/2/3 (e) monolayers ratio, bond lengths are given in Å.

Optimization of the (001) geometry of the QD surface showed that the QDs retain the original crystalline structure of the bulk materials in the core. According to the results of optimization the bond lengths on the surface are 19% shorter than in the bulk material which indicates a deviation of the surface morphology from the internal structure of the QD. It was found that all surface metal atoms are three-coordinated and have one unsaturated valency which can be used for coordination of surface agents.



Density of state maps of CdSe/CdS with 3/7 (a) and CdSe/CdS/ZnS with 3/2/5 monolayers ratio (b), band alignment for spherical CdSe/CdS (c) and CdSe/ZnS (d) QDs with core diameter 4.0 nm and shell thickness 0.5 nm.

The influence of the number of monolayers in the QD shell on the band gap was studied. For example, an increase in the number of CdS monolayers in the CdSe/CdS QD shell from 4 to 7 reduces the band gap by 13% from 2.34 eV to 2.03 eV. An increase in the number of ZnS monolayers on the CdSe/CdS/ZnS surface from 2 to 5 leads to a decrease in the band gap by 15%.

Quantum-chemical and numerical simulation methods:

- Optimization with periodic plane-wave density functional theory (DFT+U), Generalized Gradient Approximation, PBE functional, the PAW representation of the atomic cores.
- Single-point calculations with the hybrid functional HSE06 for accurate representation of the density of states and the band structure.
- The numerical simulations of band diagrams based on the solution of the multiband Schrödinger-Poisson equation in the **nextnano** software.