Quantum chemical modeling of the electronic structure of ytterbium halides by the coupled cluster method

P.A. Khadeeva[1,2], ***V.M. Shakhova***[1], ***Y.V. Lomachuk***[1], ***N.S. Mosyagin***[1], ***L.V. Skripnikov***[1,2], ***A.V. Titov***[1,2]

[1] NRC «Kurchatov Institute» - PNPI, Gatchina, Russia
[2] Saint-Petersburg State University, Saint Petersburg, Russia

Methods based on density functional theory are the most common in modeling the electronic structure of materials. However, when studying optical properties, such as excitation energies, in materials containing lanthanides and actinides, it is almost impossible to achieve reliable and high-precision results. This problem arises due to the fact that the electronic structure of such compounds has close energy levels, which leads to the need to take into account correlation and relativistic effects simultaneously. This can be achieved using relativistic coupled cluster methods, but there is a problem of necessity for time-consuming and memory-demanding calculations. To apply these approaches to crystals, our laboratory has developed a technology for cutting out a fragment from a periodic structure named CTEP (compound-tunable embedding potential) [1], which provides high accuracy in describing the influence of the environment on the selected fragment.

To analyze the correctness of reproducing the simulated electron density in the vicinity of a heavy nucleus, the chemical shift of the X-ray emission spectrum lines was chosen. For each atom, these spectra are characteristic and highly sensitive to the state of a d- or f-element in a particular compound. Direct methods for calculating the X-ray emission spectra lines are practically unapplicable, therefore a "two-step" method for its calculation was developed [2].

In this work ytterbium halides ($YbHal_n$ Hal=F, Cl, $n = 2, 3$) are investigated by a relativistic version of the CCSD. This approach has limited possibilities due to the rapid growth of its computational complexity with increasing the system size, therefore, it is important to carry out preliminary calculations on simpler systems and the stoichiometric molecules were chosen for this purpose. In the first part of the work, the calibration of the basic sets on molecular systems was carried out, which showed that when studying the "core properties" on the Yb atom, there is no need to use saturated basic sets on halogens. In the second part of the work, pilot calculations of chemical shifts of X-ray emission spectrum lines for fragments of CTEP crystals were carried out using the relativistic CCSD.

Funding Financial Support. The work was supported by the Russian Science Foundation (project No. 20-13-00225) `https://www.rscf.ru/project/23-13-45028` / NRC “Kurchatov Institute” – PNPI.

References

[1] Shakhova V. M., Maltsev D. A., Lomachuk Y. V., et al., 2022, *Phys. Chem. Chem. Phys.*, 24, 19333
[2] Lomachuk Y. V., Titov A. V., 2013, *Phys. Rev. A*, 88, 062511