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Tools for high-accuracy ab initio relativistic modeling of excited states and spectra of actinide molecules and impurity ions in solids

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Actinide compounds are among the most challenging objects for *ab initio* electronic structure modeling due to strong relativistic effects, multi-configuration nature of electronic states, and high density of levels in their spectra.

We present recently developed tools for high-precision modeling of such systems: the EXP-T program package [1] implementing new variants of the relativistic coupled-cluster method in the Fock space, the LIB-GRPP library for calculating molecular integrals with generalized relativistic pseudopotentials [2], and new approaches to calculating off-diagonal matrix elements of property operators, including those defining for intensities of electronic transitions and hyperfine effects.

Using the theoretical developments and software tools, low-lying electronic states of AcF, ThO, UO2 molecules were simulated, and information about the structure and spectra of these molecules was obtained. Term energies of the ThO molecule were obtained with errors significantly smaller than the vibrational quanta, thus allowing one to perform an unambigous vibrational assignment of its rovibronic spectra [3]. A comprehensive quantitative model of the vibronic spectrum of the AcF molecule was constructed [4], opening up possibilities for planning experiments on laser resonance ionization spectroscopy of this molecule.

The developed tools were also applied to simulate electronic spectra of cerium (Ce3+) and thorium (Th3+) impurity ions embedded into the xenotime (yttrium orthophosphate YPO4) matrix. For this purpose coupled cluster calculations were combined with the the compound-tunable embedding potential (CTEP) approach proposed recently [5] for ab initio calculations of local properties in ionic crystals via constructing minimal cluster models with broken covalent bonds. Pilot calculations were shown to be able to reproduce the energies of transitions localized on the Ce3+ impurity ion with the error not exceeding 0.3 eV.

The work of A.V.O., A.Z., Yu.V.L., N.S.M. and A.V.T. at NRC "Kurchatov Institute" –PNPI on the development of software tools and further pilot applications to ThO, AcF and xenotime was supported by the Russian Science Foundation under grant no. 20-13-00225, https://rscf.ru/project/23-13-45028/.

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