

CHEMICAL SHIFTS OF X-RAY EMISSION SPECTRA AND EFFECTIVE STATES OF YTTERBIUM IN FLUORIDES: EMBEDDED CLUSTER MODELING OF YbF_2 AND YbF_3 CRYSTALS*

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Abstract. The YbF_2 and YbF_3 crystals were studied within the embedded cluster model. The small core relativistic pseudopotentials for the central Yb atom (42 valence electrons) and embedding potentials for Yb and F atoms were constructed. Chemical shifts of $K_{\alpha 1}$ and $K_{\alpha 2}$ lines of X-ray emission spectra (XES) were calculated using non-variation one-center restoration technique and relativistic density functional theory (relDFT) with the hybrid exchange-correlation functional PBE0. It was done in the $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster simulating the YbF_3 crystal with respect to $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ one representing the YbF_2 crystal. The resulting estimates are 628 meV for $K_{\alpha 1}$ and 559 meV for $K_{\alpha 2}$ and their weighted mean agrees within 10% with the experimental value, 557 ± 27 meV. In turn, the weighted relativistic Hartree-Fock (relHF) calculation is higher on 20%. It indicates that the incorporation of electron correlation effects is essential for reproducing the $K_{\alpha 1, 2}$ chemical shifts.

Key words: XES chemical shifts, $K_{\alpha 1}$ and $K_{\alpha 2}$ X-ray emission lines, relativistic pseudopotential, relativistic density functional theory, cluster embedded in a crystal

1. INTRODUCTION

Ytterbium is one of the lanthanides with favorite valences II and III. The ground state of the ytterbium atom has the electronic configuration $[\text{Xe}] 4f146s25d0$. When the Yb atom is in the divalent state, two electrons from the outermost 6s orbital are involved in the formation of chemical bonds. In its trivalent state, one electron additionally leaves the 4f shell. Such a change of the electronic density in the spatial outer-core region (where 4f shell is localized) results in a large chemical shift (ChSh) of the characteristic X-ray emission lines (XES) on Yb. Therefore, the determination of the XES chemical shifts can be an efficient tool for studying changes in the valence states of d and f elements in a chemical compound [1]-[5].

In the present study, the theoretical modeling of the cluster embedded in the YbF_2 and YbF_3 crystals is carried out and the quantum chemical calculation of XES chemical shifts for $K_{\alpha 1}$ and $K_{\alpha 2}$ lines on ytterbium is performed.

2. PROBLEM

The XES lines of a heavy atom corresponding to electronic transitions from one inner shell to the other

one are characteristic lines for the atom. However, for the same atom in different chemical compounds (or in different valence states), these lines are slightly shifted in relation to each other. The difference between these energies of the inner-core electron transition is known as the XES chemical shift.

The XES chemical shift is a property associated with the spatial core region ("core" property [6]), which is most sensitive to changes of the electron density of valence electrons in the core region. Thus, by studying the chemical shift on an atom, we can estimate the effective valence state of this atom in the compounds under consideration. Therefore, to obtain a reasonable theoretical value of XES chemical shift we need to correctly determine the electronic density near the nucleus under study.

In the present work, the XES ChSh on ytterbium in the YbF_3 crystal compared to the YbF_2 one are evaluated via simulating the electronic structure of the crystals in the frames of the embedded cluster model with Yb as a central atom. We consider the clusters in which only the central atom and its nearest neighbors are accurately described (clusters of "minimal size" below) in order to have an opportunity to study them at different levels of correlation treatment, from the density functional theory (DFT) to the wave-function

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based methods. The main goal of this work is the development of the embedding model for the YbF_2 and YbF_3 structures for the evaluation of chemical shifts of $K_{\alpha 1, 2}$ lines.

3. COMPUTATIONAL DETAILS

3.1. Relativistic pseudopotential method

We employ the relativistic electronic structure model defined by the shape-consistent relativistic pseudopotential (RPP) method [7] for the ytterbium atom. In this paper, the valence version of the generalized RPP, vGRPP [8], [9], [10], is applied, in which the semilocal RPP operator is utilized [11].

The $4f$ shell in lanthanides is valence by energy, but it is localized in the outer-core spatial region. That leads to either the large number of explicitly treated electrons when using small-core RPP or to essentially lower accuracy for a small number of explicitly treated electrons (large-core RPP versions) in calculations of lanthanide compounds.

The goal of our study is to evaluate the XES chemical shifts, i.e. the property localized on ytterbium atom [4]. For the exact description of this property of ytterbium, we describe the atom as follows. The 28-electron innermost core, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$, is replaced by vGRPP, i.e. the small-core RPP version is assumed. The remaining (valence and outer-core) 42 electrons, which correspond to the $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^0$ configuration, are explicitly included into the calculations. We call this RPP version as 42ve-RPP below.

For fluoride atoms nearest to the central Yb, we use the all-electron model.

3.2. Theoretical study of chemical shifts of X-ray emission lines

The calculation of chemical shifts of X-ray emission lines is usually a challenging problem for modern *ab initio* methods when studying compounds containing heavy atoms including transition metals, actinides, and lanthanides. The theoretical investigation of such systems should take into account both the relativistic and correlation effects very accurately. In references [4] and [5], a method of evaluating chemical shifts of X-ray emission lines is described, which is applicable to such kind of systems. It is based on the relativistic pseudopotential model and one-center restoration approach [6] to recover a proper electronic structure in heavy-atom cores after the pseudopotential simulation of chemical compounds. An expression for chemical shift as a difference between mean values of certain one-electron effective operator is proposed there. It corresponds (in simple model cases but not generally) to the difference between the orbital energies of the initial and final shells in the compounds. It follows from [4] that the operator related to a XES chemical shifts is concentrated in the atomic core region. On the other hand, the main non-vanishing contribution to the matrix elements of this operator is due to the valence electrons, whereas the contributions from closed inner-core shells compensate each other. It has been shown

by our group (see Ref. [6] and references therein) that the procedure of evaluating such characteristics as XES chemical shifts can be significantly simplified by splitting the calculation into two steps. At the first step, the electronic correlation for valence electrons (and outer-core electrons for better accuracy) is taken into account in a molecular calculation using some method of electronic structure treatment (such as coupled cluster, configuration interaction, DFT, etc.). In turn, the core electrons (inner-core in our case with Yb) are excluded from the calculations with vGRPP [8], [9] so that an accurate electronic structure of valence region is evaluated most economically. Since the inner-core parts of the valence one-electron “pseudo-wave functions” are smoothed within the vGRPP method; they have to be recovered using some core-restoration method [6] at the second step. The non-variation restoration technique, employed in the present work, is based on approximate proportionality of valence and virtual spinors in the inner-core region of heavy atoms (see, e.g., Ref. [9] for details). The two-step approach has been recently used in references [12]–[16] for calculating various characteristics, such as hyperfine structure constants, etc. in molecules and atoms. The two-step method has been also extended to the case of crystals in Ref. [17]. Comparison of the two-step approach (in which the inner-core electrons are treated as frozen) with the all-electron treatment was made in papers [17–19], where an agreement on the level of accuracy of the used correlation methods is attained.

3.3. Modeling of the crystal structure

In our study, the experimental structural data for the crystals are used. The YbF_2 crystal has Fm-3m (225) space group and its cell parameters are $a = 0.55991$ nm, $b = 0.55991$ nm, $c = 0.55991$ nm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ [20], and the YbF_3 crystal has Pnma (62) space group and the cell parameters are $a = 0.6218$ nm, $b = 0.6785$ nm, $c = 0.4431$ nm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ [21].

We model the embedded cluster for structures of YbF_2 and YbF_3 crystals as follows. An ytterbium atom is considered as an origin in the clusters and its nearest coordination spheres are reproduced in accord to the positions of corresponding atoms in the unit cell.

Thus for the cluster simulation of the YbF_2 crystal, eight fluorine atoms are located around the central ytterbium at a distance of 0.2424 nm. They form a cube which is centered at the origin of our cluster. These fluoride atoms constitute the first coordination sphere. It is important to reproduce the electronic structure of YbF_2 within at least the “minimal cluster”, YbF_8 , around Yb in order to evaluate XES chemical shifts on Yb rather accurately. Note also that for a cluster of such size (<10 atoms) most reliable wave-function based correlation methods can be applied in principle.

Further, at 0.3959 nm distance from the center, twelve Yb atoms are located (which constitute the second coordination sphere). The next (third) coordination sphere consists of twenty four fluorine atoms at a distance of 0.4643 nm. We replace these atoms by pseudopotentials to ensure the proper embedding of the above minimal cluster into the YbF_2 crystal. Note that all these coordination spheres form

highly symmetric substructures (see Figure 1). Below, we designate this extended cluster as $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$.

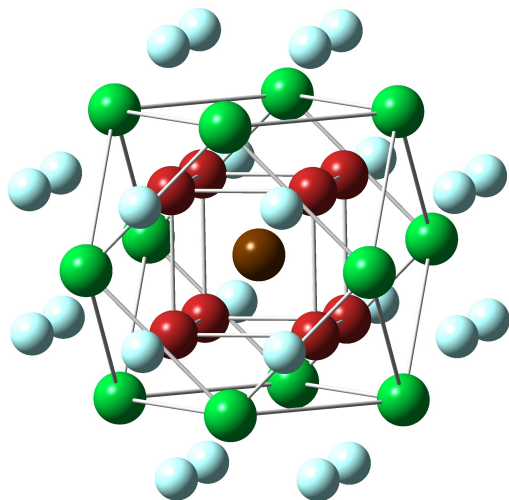


Figure 1. Structure of $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ cluster. The central Yb atom is highlighted in brown, F atoms of the first coordination sphere are red, Yb atoms of the second coordination sphere are green, and F atoms of the third coordination sphere are blue

Table 1. Distances from the center ytterbium atom for Yb and F atoms in the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ and $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ clusters, nm

Cluster	First coord. sphere	Second coord. sphere	Third coord. sphere
$\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$	Yb–F	Yb–Yb	Yb–F
	0.2424	0.3959	0.4643
Cluster $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$	First coord. region	Second coord. region	
	Yb–F	Yb–Yb	Yb–F
			0.3527
			0.3527
			0.3783
			0.3783
			0.4059
			0.4059
		0.3562	0.4157
	0.2222	0.3562	0.4190
	0.2246	0.3803	0.4190
	0.2264	0.3803	0.4190
	0.2264	0.4112	0.4190
	0.2268	0.4112	0.4310
	0.2268	0.4306	0.4352
	0.2289	0.4306	0.4352
	0.2289	0.4306	0.4424
0.2612	0.4306	0.4424	
	0.4431	0.4506	
	0.4431	0.4506	
		0.4562	
		0.4562	
		0.4657	
		0.4657	
		0.4694	
		0.4694	

The embedded cluster for the YbF_3 crystal has a more complicated structure. If we look at the area around the central atom of the order of 0.46 nm (spatially- and size-balanced with the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ cluster simulating the YbF_2 crystal), we find there 33 fluorine atoms and 12 ytterbium atoms. Below we designate this cluster as $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$. In Table 1, the distances from the center for the corresponding atoms are listed.

The first coordination sphere of $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster consists of nine fluorine atoms. It corresponds to the “minimal cluster” model, YbF_9 , for the YbF_3 crystal. The other atoms in the $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster are used to describe embedding of the YbF_9 cluster to the crystal. It is finally used to evaluate the XES chemical shifts on the central Yb.

In contrast to the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ case, we cannot uniquely identify the second and third coordination spheres (as those for atoms of the same kind) for the $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster. Nevertheless, this is the cluster that is reasonable to use in the simulation of YbF_3 crystal for the XES chemical shift evaluation (along with the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ cluster simulating YbF_2) based on the spatial- and size-balancing arguments. Thus, the second coordination region for YbF_3 crystal contains both the ytterbium and fluorine atoms. The structure of the $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster in the projections onto XY plane, XZ plane, YZ plane are shown in Figure 2.

It should be noted that both the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ and $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ clusters should be electrically neutral to avoid the unphysical charge transfer and convergence problems [22]. The simplest way to satisfy this is to model the same atoms in different coordination spheres by different ways.

As noticed above, the central ytterbium atom in the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ cluster is described by the 42ve-RPP. The atom has an oxidation state +2. The basis sets (10s10p7d7f2g)/ [9s8p5d4f2g] for ytterbium compatible with the vGRPP was generated aimed for the relDFT calculations of Yb compounds.

Eight fluorine atoms of the first coordination sphere are included in the calculations with all electrons treated explicitly and aug-cc-pVTZ basis set was used for them [23]. The minimum cluster YbF_8 has a formal charge of -6. Consequently, the remaining atoms of the $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ cluster must compensate this charge for electrical neutrality. So we simulate (an average) charge of +1.5 on each of twelve ytterbium atoms from second coordination sphere that roughly corresponds to a partial charge on Yb in the YbF_2 compounds [24]. They are described by the 2ve-RPP (generated for the $[\text{Xe}4f^{14}]6s^{0.16}p^{0.15}d^{0.15}f^{0.15}g^{0.1}$ configuration) with the reduced effective nuclear charge (from +2 to +1.5) and minimal basis set (4s4p4d) used on these atoms. The fluorine atoms from the third coordination sphere are treated in the form of point-nuclei with effective charges of -0.5 (to satisfy the electroneutrality of the cluster) with minimal basis set (3s)/[2s] on them which corresponds to 3-21G basis set for H atom [25].

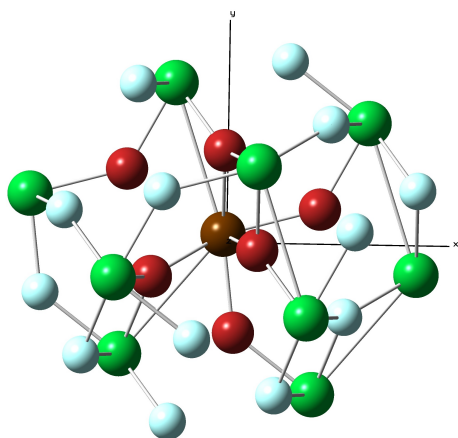


Figure 2a. Structure of $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster projected on the XY plane. The designations are equivalent to those in Figure 1

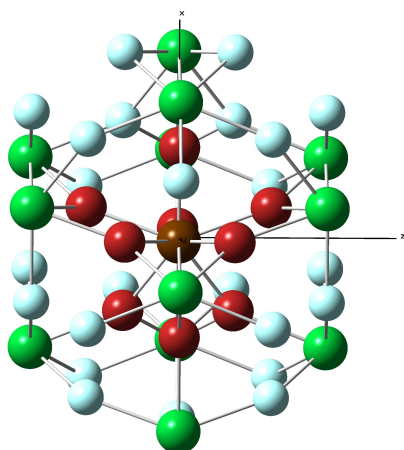


Figure 2b. Structure of $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster projected on the XZ plane. The designations are equivalent to those in Figure 1

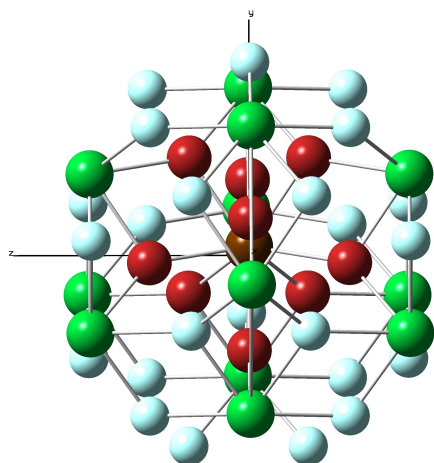


Figure 2c. Structure of $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster projected on the YZ plane. The designations are equivalent to those in Figure 1

Now we consider the embedded cluster simulation of YbF_3 . In the case of $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster, we use

particularly generated pseudopotential and basis set for Yb atoms from the second coordination region and different effective charge on Yb and F atoms from this region. The cluster of minimal size, YbF_9 , has a total charge -6 like a minimal cluster YbF_8 . The charges on twelve ytterbium atoms are chosen as $+2.5$, which roughly (in average) correspond to partial charges on Yb in the YbF_3 compounds [24]. These atoms are described by 3ve-RPP for ytterbium (generated for the $[\text{Xe}4f^{13}]5d^{0.66}5s^{0.16}p^{0.1}$ configuration with the open $4f$ shell treated as a core shell, i.e. excluded from the explicit treatment). The effective nuclear charge was correspondingly reduced from $+3$ to $+2.5$. The basis set (7s5p3d) on these atoms was used. The twenty four fluorine atoms have a charge -1 and thus the electroneutrality of the cluster is satisfied.

4. RESULTS AND DISCUSSIONS

The calculations are performed within relHF and relDFT using the hybrid exchange-correlation functional PBE0 that comprise 25% of the Hartree–Fock exchange [26], [27]. The computer code [28] was used.

The non-variation restoration code developed in references [14], [17], [29], [30] was used to obtain the correct four-component electronic wave function near the Yb nucleus. Chemical shifts of $K_{\alpha 1, 2}$ lines were calculated at experimental structural data [20], [21] by the method described in [4], assuming the core restoration radius $R_c = 0.55$ a.u. (see Table 2). The experimental value for the chemical shift of K_{α} lines for the YbF_3 crystal with respect to the YbF_2 one was taken from Ref. [31] (the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines were not resolved in the experiment).

Table 2. Computed chemical shifts of $K_{\alpha 1}$ and $K_{\alpha 2}$ lines for $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster with respect to $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ cluster, meV

Method	$K_{\alpha 1}$	$K_{\alpha 2}$	Weighted mean $K_{\alpha}^{\text{theor}}$
relHF	702	627	677
relDFT/PBE0	628	559	605
Exp. [31]	557±27		

One can see that the PBE0 values are in a better agreement with the experimental data than the RHF ones that indicates the importance of accounting for correlation effects.

In order to compare our values with the experimental one, we use a weighted mean $K_{\alpha}^{\text{theor}} = (2 K_{\alpha 1} + K_{\alpha 2})/3 = 605$ meV (relDFT/PBE0), that agrees with the experiment within *ca.* 10%. The relHF method yields $K_{\alpha}^{\text{theor}} = 677$ meV overestimating the experimental datum by more than 20%.

5. CONCLUSIONS

The environments of Yb atoms in YbF_2 and YbF_3 crystals are simulated within a cluster model using embedding potential technique. Both RPPs and embedding potentials for Yb and F atoms were constructed. The cluster model allows one to use different levels of correlation treatment, from DFT to

the coupled cluster one, and flexible basis sets for better control of the computational accuracy. The application of the latter is planned in further studies.

The chemical shifts for $K_{\alpha 1}$ and $K_{\alpha 2}$ lines in the $\text{YbF}_9\text{Yb}_{12}\text{F}_{24}$ cluster with respect to $\text{YbF}_8\text{Yb}_{12}\text{F}_{24}$ were calculated using the relHF method and relDFT with the hybrid functional PBE0.

The weighted mean of computed PBE0 chemical shifts for K_{α} lines agree within 10% with experimental datum that we consider as a good result, whereas the neglect of electron correlations within the relHF approximation leads to the overestimation of the chemical shift by more than 20%.

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REFERENCES

1. K. Siegbahn, "From X-Ray to Electron Spectroscopy," in *Lecture Notes in Physics: Nishina Memorial Lectures*, vol. 746, Osaka, Japan: Springer, 2009, ch. 8, pp. 137 – 228.
DOI: 10.1007/978-4-431-77056-5_8
2. O. I. Sumbaev, "Shift of K X-ray lines associated with valency change and with isomorphous phase transitions in rare earths," *Phys. Usp.*, vol. 21, no. 2, pp. 141 – 154, 1978.
DOI: 10.1070/PU1978v021n02ABEH005519
3. R. I. Karaziya, A. I. Udris, D. V. Grabauskas, "Use of the Chemical Shifts of Electron Levels in the Study of the Distribution of the Effective Charges of Atoms in Compounds," *J. Struct. Chem.*, vol. 18, no. 4, pp. 520 – 525, 1977.
DOI: 10.1007/BF00745283
4. Y. V. Lomachuk, A. V. Titov, "Method for Evaluating Chemical Shifts of X-ray Emission Lines in Molecules and Solids," *Phys. Rev. A*, vol. 88, 062511, 2013.
DOI: 10.1103/PhysRevA.88.062511
5. A. V. Titov, Y. V. Lomachuk and L. V. Skripnikov, "Concept of effective states of atoms in compounds to describe properties determined by the densities of valence electrons in atomic cores," *Phys. Rev. A*, vol. 90, 052522, Nov. 2014.
DOI: 10.1103/PhysRevA.90.052522
6. A. V. Titov, N. S. Mosyagin, A. N. Petrov, T. A. Isaev, D. P. DeMille, "Study of P,T-parity violation effects in polar heavy-atom molecules," in *Progress in Theoretical Chemistry and Physics: Recent Advances in the Theory of Chemical and Physical Systems*, vol. 15, J.-P. Julien, J. Maruani, D. Mayou, S. Wilson, G. Delgado-Barrio, Eds., Dordrecht, Netherlands: Springer, 2006, ch. 12, pp. 253–283.
DOI: 10.1007/1-4020-4528-X_12
7. P. A. Christiansen, Y. S. Lee and K. S. Pitzer, "Improved ab initio effective core potentials for molecular calculations," *J. Chem. Phys.*, vol. 71, no. 11, pp. 4445–4450, 1979.
DOI: 10.1063/1.438197
8. N. S. Mosyagin, A. V. Zaitsevskii and A. V. Titov, "Shape-consistent relativistic effective potentials of small atomic cores, international review of atomic and molecular physics," *Int. Rev. At. Mol. Phys.*, vol. 1, no. 1, pp. 63 – 72, 2010.
Retrieved from:
<https://pdfs.semanticscholar.org/82f5/65187ec338407439d7cb111e58e53adfc19c.pdf>
9. A. V. Titov and N. S. Mosyagin, "Generalized relativistic effective core potential: Theoretical grounds," *Int. J. Quantum Chem.*, vol. 71, no. 5, pp. 359 – 401, 1999.
DOI: 10.1002/(SICI)1097-461X(1999)71:5<359::AID-QUA1>3.0.CO;2-U
10. N. S. Mosyagin, A. V. Zaitsevskii, L. V. Skripnikov, A. V. Titov, "Generalized relativistic effective core potentials for actinides," *Int. J. Quantum Chem.*, vol. 116, no. 4, pp. 301 – 315, Feb. 2016.
DOI: 10.1002/qua.24978
11. A. V. Titov and N. S. Mosyagin, "Generalized relativistic effective core potential method: Theory and calculations," *Russ. J. Phys. Chem.*, vol. 74, suppl. 2, pp. S376 – S387, 2000.
Retrieved from:
<https://arxiv.org/pdf/physics/0008160.pdf>
Retrieved on: Aug. 5, 2017
12. L. V. Skripnikov, A. N. Petrov, A. V. Titov, N. S. Mosyagin, "Electron electric dipole moment: Relativistic correlation calculations of the P,T-violation effecting the $^3\Delta_3$ state of PtH^+ ," *Phys. Rev. A*, vol. 80, no. 6, 060501(R), Dec. 2009.
DOI: 10.1103/PhysRevA.80.060501
13. L. V. Skripnikov, A. V. Titov, A. N. Petrov, N. S. Mosyagin, O. P. Sushkov, "Enhancement of the electron electric dipole moment in Eu^{2+} ," *Phys. Rev. A*, vol. 84, no. 2, 022505, Aug. 2011.
DOI: 10.1103/PhysRevA.84.022505
14. A. N. Petrov, "Hyperfine and Zeeman interactions of the $a(1)[^3\sigma_1^+]$ state of PbO ," *Phys. Rev. A*, vol. 83, no. 2, 024502, Feb. 2011.
DOI: 10.1103/PhysRevA.83.024502
15. J. Lee et al., "Optical spectroscopy of tungsten carbide for uncertainty analysis in electron electric dipole moment search," *Phys. Rev. A*, vol. 87, no. 2, 022516, Feb. 2013.
DOI: 10.1103/PhysRevA.87.022516
16. A. N. Petrov, L. V. Skripnikov, A. V. Titov, R. J. Mawhorter, "Centrifugal correction to hyperfine structure constants in the ground state of lead monofluoride," *Phys. Rev. A*, vol. 88, no. 1, 010501(R), Jul. 2013.
DOI: 10.1103/PhysRevA.88.010501
17. L. V. Skripnikov, A. V. Titov, "LCAO-based theoretical study of PbTiO_3 crystal to search for parity and time reversal violating interaction in solids," *J. Chem. Phys.*, vol. 145, no. 5, 054115, Aug. 2016.
DOI: 10.1063/1.4959973
18. L. V. Skripnikov, "Combined 4-component and relativistic pseudopotential study of ThO for the electron electric dipole moment search," *J. Chem. Phys.*, vol. 145, no. 21, 214301, Dec. 2016.
DOI: 10.1063/1.4968229
PMid: 28799403
19. L. V. Skripnikov, A. D. Kudashov, A. N. Petrov, A. V. Titov, "Search for parity- and time-and-parity-violation effects in lead monofluoride (PbF): Ab initio molecular study," *Phys. Rev. A*, vol. 90, no. 6, 064501, Dec. 2014.
DOI: 10.1103/PhysRevA.90.064501
20. T. Petzel, O. Greis, "The vaporization behavior of ytterbium(III) fluoride and ytterbium(II) fluoride," *J. Less-Common Met.*, vol. 46, no. 2, pp. 197 – 207, May 1976.
DOI: 10.1016/0022-5088(76)90210-1
21. B. V. Bukvetskii, L. S. Garashina, "Crystal-Chemical Investigation of the Orthorhombic Trifluorides of Samarium, Holmium, and Ytterbium," *Sov. J. Coord. Chem.*, vol. 3, pp. 791 – 795, 1977.
22. I. V. Abarenkov, M. A. Boyko, "Wave-Function-Based Embedding Potential for Ion-Covalent Crystals," *Int. J. Quantum Chem.*, vol. 116, no. 3, pp. 211 – 236, Feb. 2016.
Retrieved on: Aug. 5, 2017

- DOI: 10.1002/qua.25041
23. R. A. Kendall, T. H. Dunning, Jr. and R. J. Harrison, "Electron affinities of the first-row atoms revisited: systematic basis sets and wave functions," *J. Chem. Phys.*, vol. 96, no. 9, 6796, May 1992.
DOI: 10.1063/1.462569
 24. S. G. Semenov, M. E. Bedrina, A. V. Titov, "Quantum-chemical Study of Ytterbium Fluorides and of Complex $F_2YbF_2CeF_2$," *Russ. J. Gen. Chem.*, vol. 86, no. 6, pp. 1215 – 1220, Jun. 2016.
DOI: 10.1134/S1070363216060013
 25. J. S. Binkley, J. A. Pople, W. J. Hehre, "Self-Consistent Molecular Orbital Methods. 21. Small Split-Valence Basis Sets for First-Row Elements," *J. Am. Chem. Soc.*, vol. 102, no. 3, pp. 939 – 947, Jan. 1980.
DOI: 10.1021/ja00523a008
 26. J. P. Perdew, K. Burke, M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865 – 3868, 1996.
DOI: 10.1103/PhysRevLett.77.3865
PMid: 10062328
 27. C. Adamo, V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *J. Chem. Phys.*, vol. 110, no. 13, pp. 6158 – 6170, Apr. 1999.
DOI: 10.1063/1.478522
 28. C. van Wuelen, "A quasirelativistic two-component density functional and Hartree-Fock program," *Z. Phys. Chem.*, vol. 224, no. 3-4, pp. 413 – 426, 2010.
DOI: 10.1524/zpch.2010.6114
 29. L. V. Skripnikov, A. V. Titov, "Theoretical study of ThF^+ in the search for t,p-violation effects: Effective state of a Th atom in ThF^+ and ThO compounds," *Phys. Rev. A*, vol. 91, no. 4, 042504, Apr. 2015.
DOI: 10.1103/PhysRevA.91.042504
 30. L. V. Skripnikov, A. N. Petrov and A. V. Titov, "Communication: Theoretical study of ThO for the electron electric dipole moment search," *J. Chem. Phys.*, vol. 139, no. 22, 221103, Dec. 2013
DOI: 10.1063/1.4843955
PMid: 24329049
 31. В. А. Шабуров и др, "Состояния промежуточной валентности иттербия в интерметаллических соединениях," т. 24, no. 1, стр. 263 – 265, 1982. (V. A. Shaburov et al., "State of the intermediate valence ytterbium in intermetallic compounds," *Phys. Solid State*, vol. 24, no. 1, pp. 263–265, 1982.)