Benchmark *ab initio* study of heavy- and superheavy-element systems

A.V. Titov,* N.S. Mosyagin, A.N. Petrov, and T.A. Isaev

The main direction of research of our group is development of *ab initio* methods for very accurate investigation of electronic structure of heavy and superheavy elements as well as molecules containing such elements and benchmark calculations [1]. This activity is stimulated by impressive progress in atomic and molecular experiments during last years probing fundamental phenomena with unique sensitivity. Mention only advances in studying P,T-parity nonconservation (PNC) effects in molecules and discovery of superheavy elements from "island of stability". Success in trapping and cooling atoms and molecules brought in a new epoch in control over these systems which may not exist in other conditions. The planning, execution and interpretation of these experiments depend critically on atomic and molecular data, which can only be obtained theoretically.

During last five years, further development of the generalized relativistic effective core potential (GRECP) [2, 3] and e-center restoration methods [3–5] earlier suggested by us was continued. In particular, GRECP versions accounting for correlations with core electrons [6] and quantum electrodynamic (Breit) effects and Fermi model for nuclei were first generated for the eka-Hg (E112), eka-Tl (E113), eka-Pb (E114), U, Pu [7, 8], and other atoms [1]. It was shown in the above papers that accuracy of the generated GRECPs is about an order of magnitude higher than that of the RECPs of other groups for the case of the same number of explicitly treated electrons when outer core shells are treated explicitly. The GRECPs allow one to attain reliably the level of the "chemical accuracy" (about 1 kcal/mol or 350 cm^{-1}for transition energies) with moderate computational efforts.

A new flexible scheme for optimal basis set generation was suggested [9, 10]. Some improvements in relativistic coupled cluster with single and double cluster amplitudes (RCCSD) [11, 12] and configuration interaction [13, 14] methods, particularly, their combination to account for outercore-valence correlations and higher-order effects were implemented [10, 15, 16]. Besides, a number of codes for calculation of atomic and molecular properties were written and combined with the RCCSD package of U.Kaldor and SODCI one of R.Buenker groups.

The developed methods and combined codes allowed us to perform a series of benchmark atomic and molecular calculations with heavy and superheavy elements of both core (PNC, HFS) and valence (spectroscopic) properties. First of all, we investigated the influence of polarization and correlation effects on enhancement of P,T-odd properties in molecules of primary interest for the PNC experiments. In particular, our group first calculated the restriction on the proton electric dipole moment (EDM) given by E. Hinds *et al.* with accounting for correlations within the RCCSD method [12]. Our data are also required for the corresponding experiment prepared at PNPI. The first reliable calculations of the effective field on the electron in the metastable $a(1)$ state of the PbO molecule were performed [16, 17] since PbO is used now in the experiment on search for the electron EDM by the group of D. DeMille. Recently, a new scheme for the electron EDM search on the HI$^+$ molecular ion was suggested by R. Stutz and E. Cornell. As our extensive calculations of electron EDM enhancement factor showed, that ion is not the best possible candidate for EDM search in experiments of the novel type [18], however, the experiments on molecular ions allow one to extend drastically the variety of systems for measurement. It is important to notice, that the PNC enhancement is increased by an order of magnitude due to the polarization-coorelation effects in such systems as PbO* and HI$^+$.

The first results of relativistic correlation calculation of the spectroscopic properties for the ground state of E112H and its cation are also obtained in which spin-orbit interaction is taken into account nonperturbatively. Studying the properties of superheavy element 112 in comparison with its lighter analogue Hg[19] is required for reliable chemical identification of its long-lived isotope, ^{283}112, first of all. It is shown that appropriate accounting for the spin-orbit effects leads to dramatic change of spectroscopic properties of E112H whereas they are not so important for E112H$^+$. Our results indicate that E112 should not be expected as "more inert" than Hg in opposite to that suggested earlier.

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* URL: `http://www.qchem.pnpi.spb.ru`

[1] Titov A.V. et al. *Phys. At. Nucl.*, 2003. **66**, 1152.
[2] Titov A.V., Mosyagin N.S. *Russ.J.Phys.Chem.*, 2000. **74,** Suppl. 2, S376.
[3] Titov A.V. *Doctorate Thesis*, (PNPI RAS, Russia, 2002).
[4] Titov A.V. et al. *Int. J. Quant. Chem.*, 2005. **104**, 223.
[5] Titov A.V. et al. *PTCP*, 2005; arXiv: physics/0506038.
[6] Mosyagin N., Titov A. *J.Chem.Phys.* 2005. **122**, 234106.
[7] Petrov A.N. et al. *J. Phys. B*, 2004. **37**, 4621.
[8] Mosyagin N. et al. *PTCP*, 2005; arXiv: physics/0505207.
[9] Mosyagin N.S. et al. *J. Phys. B*, 2000. **33**, N 4, 667.
[10] Isaev T.A. et al. *J. Phys. B*, 2000. **33**, N 22, 5139.
[11] Mosyagin N.S. et al. *J. Phys. B*, 2001. **34**, N 3, 339.
[12] Petrov A.N. et al. *Phys. Rev. Lett.*, 2002. **88**, N 7, 073001.
[13] Titov A.V. et al. *Int. J. Quant. Chem.*, 2001. **81**, 409.
[14] Mosyagin N.S. et al. *Int. J. Quant. Chem.*, 2002. **88**, 681.
[15] Isaev T.A. et al. *Int. J. Quant. Chem.*, 2002. **88**, 687.
[17] Isaev T.A. et al. *Phys. Rev. A*, 2004. **69**, 030501(R).
[16] Petrov A.N. et al. *Phys. Rev. A*, 2005. **72**, 022505.
[18] Isaev T.A. et al. *Phys. Rev. Lett.*, 2005, in press; ArXiv: physics/0412177.
[19] Mosyagin N.S. et al. *J. Chem. Phys.*, 2001. **115**, 2007.