First-principles relativistic calculations of the magnetic properties of lanthanide complexes: are quantitative predictions possible?

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Lanthanides are of fundamental importance in contemporary chemistry and for applications in materials science. In particular, lanthanides have become the corner-stone components of molecule-based functional magnetic materials due to their large magnetic moments, large anisotropies, and slow relaxation [1]. Recently, a breakthrough in the field of single-molecular magnetism occurred when the blocking temperature of the dysprosium metallocenes exceeded the temperature of liquid nitrogen [2]. The growing amount of detailed experimental data requires the high-level quantum chemical calculations to understand temperature dependences of the magnetic susceptibility and relaxation of magnetization of the single-molecule magnets (SMMs) and to establish the relationship of their chemical structure with magnetic and relaxation properties.

In the case of lanthanides, a correct account for relativistic effects is essential. Therefore, we performed high-level SA-CASSCF and CASPT2 calculations accompanied by a non-perturbative account of the spin-orbit coupling (SOC). This report will present and discuss the results of calculations for a number of lanthanide complexes: single-ion magnets (SIM) and dinuclear SMMs containing lanthanide and 3d-metal cations. The calculation results, namely wave functions and energies of the magnetic sublevels, are used to calculate magnetic susceptibility and magnetization, spin-Hamiltonian parameters for pseudo-spin states, matrix elements of the transition magnetic moments between lowest-energy magnetic sublevels, etc. The latter data are used to model and explain the results of the static and dynamic measurements, which will be demonstrated using the experimental results of our colleagues and literature data.

Even more complicated problem is understanding and modelling the properties of lanthanide complexes with paramagnetic ligands, which are also promising as SMMs [1]. The report will also present and discuss results of the calculations for lanthanide complexes with radical anions [3].

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