Theoretical studies of Ni^{2+} complexes (*S* = 1) with a low zero-field splitting

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Molecular quantum bits (qubits) have the advantage of a bottom-up, controlled design tunable for specific applications. Transition metal complexes with a triplet ground state (S = 1) serve as promising electronic spin qubit candidates. In this work, I present results from theoretical studies of energies and properties of octahedral (O_h) Ni(II) complexes with strong-field ligands. Deviation from the perfect O_h symmetry results in the splitting of the ground state into three sublevels, M_s = 0 and M_s = ± 1. Energy differences between the sublevels are defined by the zero-field splitting (ZFS) parameters D and E. The small positive D values correspond to a stabilization of the M_s = 0 relative to M_s = ± 1 sublevels. The soft coordination environment around the metal center is key to ensuring low D, which is a desired quality for optical initialization and readout of qubits. *Ab initio* calculations are performed to describe the ground and excited states of Ni^{2+} complexes. I employ complete active space self-consistent field (CASSCF) method with dynamic correlation corrections from the second-order n-electron valence state perturbation theory (NEVPT2). Two active space sizes are considered: a smaller one with $3d^8$ electrons of Ni^{2+} (8,5) and a larger one with 12 electrons in 12 orbitals (12,12), where two highest Ni-ligand σ bonding and Ni 4d-orbitals are added. Independently of the active space, the singly occupied σ anti-bonding Ni-ligand orbitals of the ground state have considerable ligand character indicating that D is indeed expected to be low. The calculations provide insight into the magnitude and sign of D, as well as the nature of contributions from various excited states. Namely, the main contributions to D stem from the lowest energy excited triplet and the third excited singlet states of the Ni^{2+} complexes. Overall, the calculations confirm that Ni^{2+} (S = 1) complexes are suitable candidates for electronic spin qubits.