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Title:	AB INITIO MODELING OF MOLECULAR MAGNETS
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Abstract:	<p>A surge toward the miniaturization of quantum technological devices has brought a burst of research in the field of molecular magnetism. Molecular magnets manifest promising applications in spin qubits and high-density data storage devices. However, obtaining such molecules that exhibit exotic magnetic properties at room temperature is the key challenge that limits its practical applications. First-principle based quantum chemical calculations provide a way to design and screen such magnetic molecules that will operate at finite temperatures. In this context, we have computationally investigated the magnetic properties of organometallic complexes that possess large magnetic anisotropy and are generally known as single-molecule magnets, along with metal-free organic molecular magnets that exhibit substantial isotropic ferromagnetic exchange interactions. Single-molecule magnets (SMMs) are magnetically bi-stable molecules exhibiting slow relaxation of magnetization, which is characterized by an energy barrier, U_{eff}, to magnetic moment reversal. Although the field is primarily dominated by 4f systems due to large spin-orbit coupling in the lanthanides, the research on transition metal complexes has recently gained momentum due to their potential to create strongly coupled spin systems which is in complete contrast to the lanthanides complexes. In transition metal complexes, the large magnetic anisotropy is achieved by complexes exhibiting unquenched first-order orbital angular momentum which is manifested by complexes with high axial symmetry or low coordination numbers. Moreover, the transition metal complexes also show the phenomenon of spin-crossover brought out by the application of some external stimuli like temperature, pressure, magnetic field, etc. In this thesis, we have studied axially symmetric complexes in the presence and absence of equatorial ligands to obtain insights into magnetic anisotropy and spin-crossover properties employing density functional theory and multireference (e.g., CASSCF/NEVPT2) methods. In this regard, firstly the trigonal bipyramidal complexes based on Fe(III) are studied to probe the effect of the ligand environment on the ground-spin state and magnetic anisotropy of the complexes. Additionally, these complexes are stabilized in an intermediate spin as the ground state and are found to exhibit a high spin excited state in close vicinity of the ground state and thus are investigated for spin-crossover properties. It has been observed that magnetic anisotropy is significantly influenced by axial ligands. From these observations, we further advanced our studies to the more exotic systems based on Fe(I) bearing explicitly axial ligands. These systems provide enhancement in the magnetic anisotropy due to large unquenched orbital angular momentum. Thus, molecular engineering by the systematic reduction in the coordination number is proposed as a suitable strategy to enhance the magnetic anisotropy in the transition metal based SMMs. Organic molecular magnets (OMMs) are magnetic materials in which the spin-carriers are based on organic moieties. Open-shell organic diradicals with large isotropic ferromagnetic exchange interactions, high-spin ground-states, and persistent stability at room temperature are the holy grail of OMMs. In this thesis, we aim to design organic diradicals with strong ferromagnetic exchange interactions and a high-spin ground state based on stable radicals. In this context, at first, we studied the electronic structure of one of the super-stable, Blatter's radical. The unique delocalization of the spin density among the three nitrogen atoms provides the merostabilization to the radical. Subsequently, based on this radical, several diradicals are designed with the sole aim to enhance the magnetic exchange interactions. It has been observed that due to the delocalization of spin density on the three nitrogen atoms, the three micromagnetic centers are created at each radical center giving rise to a total of nine possible exchange pathways in the diradicals and the resultant of these multiple pathways provided the nature of exchange in the diradical. Additionally, we provided a unique strategy to tune the inherent diamagnetic zwitterionic ground-state of tetraphenylhexaazaanthracene (TPHA), a molecule embracing two Blatter's monomers, to antiferro- and ferromagnetically coupled diradicals by systematically increasing the length of the coupler between the two radical moieties.</p>
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