CAS-DFT approach to the ligand field theory

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In recent investigations of low-lying states of transition metal complexes and metal oxides, the time-dependent (TD) density functional theory (DFT) is usually employed. However, when we treat the low-lying states of open-shell species, TD-DFT often suffers the negative excitation energy, implying that the single-determinant solution is unstable for some first-order variation.

Previously, we present simple CAS-DFT approaches for degenerate and nearly degenerate systems. In this method, we do not employ any auxiliary variables, but employ the effective CASCI-DFT and CASSCF-DFT equations for the ground and excited states in order to satisfy the variational principle for both ground and excited states. As a continuation of previous studies, we investigate the transition metal complexes $V(III)L_6$, $Cr(III)$ L_6 (L = H_2O and CO), $Fe(II)L_4$ (L = ^-SH). Our CAS-DFT computations yield reasonable potential surfaces of several low-lying spin states, which are fully compatible with the experimental results and also with those of ligand field theory. Then, we estimated Racah parameters and Slater-Condon factors from the calculated energy diagrams. Implications are discussed from the viewpoint of further applications of spectrum of metal complexes

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