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**Constraint density functional calculations for multiplets in ligand-fields: Applications to Fe-phthalocyanine and  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$**  Y. KITAOKA, K. NAKAMURA, T. AKIYAMA, T. ITO, Mie University, M. WEINERT, University of Wisconsin-Milwaukee, A.J. FREEMAN, Northwestern University — In transition-metal-based complexes and molecules, multiplet structures are essential in understanding the electronic structure. However, it is often difficult to evaluate a *true* ground state or the *lowest* state within a given ligand (or crystal) symmetry from first principles calculations based on density-functional theory (DFT). Here, we propose a simple DFT approach, implemented into the FLAPW method<sup>2</sup>, to treat multiplets in ligand-fields, by imposing a density matrix constraint on the *d*-orbital occupation numbers. We demonstrate the utility of this approach for the case of an isolated single Fe phthalocyanine (FePc) and a Cr impurity in a corundum  $\text{Al}_2\text{O}_3$ . For the FePc, results predict that there are three stationary states of  ${}^3E_g$ ,  ${}^3B_2$ , and  ${}^3A_2$  in the  $\text{Fe}^{2+}$  ion, and our total energy calculations clearly demonstrate that the ground state is  ${}^3A_{2g}$ . In the case of the  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ , where an on-site Coulomb correlation correction ( $+U$ ) is incorporated, the ground state is  ${}^4A_2$  and the total energy difference between the ground state and the excited state  ${}^4T_2$ , 2.9 eV, roughly agrees with an experimental value of 2.23 eV.

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<sup>2</sup>Wimmer, Krakauer, Weinert, Freeman, PRB**24**, 864; Weinert, Wimmer, Freeman, PRB**26**, 4571

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