Effective Hamiltonian of Crystal Field Method for Periodic Systems Containing Transition Metals

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Effective Hamiltonian of Crystal Field (EHCF) is a hybrid quantum chemical method originally developed[1,2] for an accurate treatment of highly correlated *d*-shells in molecular complexes of transition metals. In the present work, we have extended the EHCF method to periodic systems containing transition metal atoms with isolated *d*-shells, either as a part of their crystal structure or as point defects. A general solution has been achieved by expressing the effective resonance interactions of an isolated *d*-shell with the band structure of the crystal in terms of the Green's functions represented in the basis of local atomic orbitals.[3,4] Such representation is valid for perfect crystals and for periodic systems containing atomic scale defects.

Our test results[3] for transition metal oxides, such as MnO, FeO, CoO, NiO, and MgO periodic solid containing transition metal impurities, demonstrate the ability of the EHCF method to accurately reproduce the spin multiplicity and spatial symmetry of the ground state,[3] and are in a good agreement with experimentally observed *d-d* transitions in optical spectra. We have also applied the developed method to carbodiimides of transition metals (CuNCN, FeNCN, CoNCN, MnNCN), which possess interesting magnetic properties and are well studied experimentally[5,6] thus allowing for detailed testing of our theoretical predictions against experimental benchmarks.

Finally, future perspectives of the EHCF and its place in the context of modern solid state quantum chemistry and physics will be discussed.

References

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