Thermodynamic Description of Spin-Crossover Materials with the Mean Value Ensemble Hubbard-U Correction

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Spin-crossover materials are constituted of molecules capable of switching reversibly from a low- (LS) to a high-spin (HS) state under the stimulus of an external perturbation such as temperature, pressure, light, guest molecules, electric field, etc. [P. Gütlich and H. A. Goodwin in *Spin crossover in transition metal compounds* (Springer: Berlin and New York, 2004)]. Proper description of the spin conversion requires the calculation of an accurate energy difference, $\Delta E_{HL} = E_{HS} - E_{LS}$, between those spin states. In the context of density functional calculations, overestimated ΔE_{HL} values often arise from common generalized, and meta-generalized, gradient exchange-correlation approximations. Inclusion of single determinant exchange contributions or Hubbard-U terms often is used to compensate. The drawback is that these approaches can easily overcorrect energy differences and result in unrealistic negative spin-crossover energies [Comput. Mat. Sci. **206**, 111161 (2022)].

This work focuses on using a novel ensemble-average determination of a Hubbard-U correction on a reference spin-state constituted of a linearly mixed LS-HS configuration. Based on data for a set of twenty spin-crossover materials [Inorg. Chem. **57**, 14097 (2018)], we demonstrate that the method improves adiabatic total energy differences, thereby providing a better description of the thermally driven spin conversion of crossover aggregates. Our findings suggest that use of these U values alleviates the overestimation of transition temperatures by nearly an order of magnitude compared to uncorrected calculations using a common generalized gradient approximation [Phys. Rev. Lett. **77**, 3865 (1996)].

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