

Hybrid Density Functional Methods for Transition Metal Clusters: Scaling Relations and Adsorption of Molecules

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A DFT description of adsorption processes on transition metal clusters by non-empirical hybrid functionals like PBE0, is promising because these methods may provide a more accurate thermochemistry due to a reduced self-interaction error. Yet, correcting the self-interaction error by a partial admixture of exact exchange to the exchange functional may worsen the description of the electronic structure of metallic systems.

To assess the accuracy provided by hybrid DFT methods for metal clusters, we examined highly symmetric platinum clusters that exhibit structural features of the bulk material. Results for a series of Pt_n nanoparticles ($n = 13, 38, 55, 79, 147$) were extrapolated and compared to the corresponding properties of Pt bulk. This study extended previous work on palladium nanoclusters where this modeling strategy was used to examine local and semi-local exchange-correlation functionals [1–2].

Larger cuboctahedral metal clusters have successfully been employed for modeling atomic and molecular adsorption on metal nanoparticles [3–5]. Therefore, in a second instance, we used some of the larger Pt clusters to model CO adsorption at various sites (top, bridge, hollow). We examined hybrid functionals for their ability to predict the correct site preference for CO adsorption, an ongoing problem of DFT methods.

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