Estimation and Correction of Spin Contamination Errors on Surface Reactions: Application of Approximate spin Projection method to UDFT/PAW method

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It is well-known that unrestricted density functional theory (UDFT) calculation includes a spin contamination error when it has a broken symmetry state. For the investigation of catalytic reactions, the states participate in radical dissociation reactions and reactions of open shell molecules that are usually important processes of catalytic reactions, such as rate-determining process, therefore the spin contamination in the catalytic reactions sometimes cause crucial errors in estimation of the activation barriers. For instance, prior works have argued that correction of spin contamination error affects the energies and geometries of catalytic reactions by homogeneous catalysts, enzymes, and noble metal clusters.[1-3] On the other hand, the effects of spin contamination error in heterogeneous catalysts are still unclear. This is because there is no scheme for correction and estimation of spin contamination error in total energy estimated by UDFT/plane-wave method.

In the present work, we have succeeded in correcting the spin contamination error in DFT calculations for a surface reaction via the application of the approximate spin projection (AP) scheme[4] to UDFT with the projector-augmented plane-wave basis (UDFT/PAW) method[5]. We show the result of dissociative adsorption of Au_2 onto MgO (001) for example. The restricted low spin state, high spin state, and broken symmetry state (low spin) were calculated, and the broken symmetry state was the ground state. The spin density plot and atomic magnetic moments of Au atoms were shown in Fig. 1. It is clear that the spin is polarized and is localized on Au-O fragment. The 0.06 eV of spin contamination error was confirmed in this system.

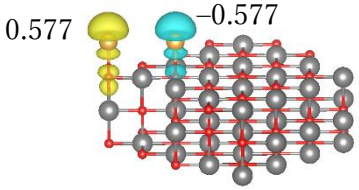

Fig. 1 Spin density plot of 2Au/MgO system. The numbers in figure indicate atomic magnetic moments of Au atoms.

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