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Theoretical study of combined plane wave and localized orbital electronic structure calculations for material design

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The demand is growing for more accurate first-principles calculations that are applicable for larger and realistic systems. The hybrid quantum mechanical/molecular mechanics (QM/MM) method which is used in quantum chemical calculations based on the localized orbital (LO) approach enables the investigation of chemical processes in larger molecular systems. However, sometimes this approach does not fully reproduce the electronic structure and geometry, such as surface or bulk systems. A large number of application have been reported for plane wave (PW) based on first-principles calculations with periodic boundary condition (PBC) for bulk, surface, and interface models. Compared with LO based approach, the PW based approach can be applied to large systems and can describe the delocalized electrons in a PBC framework. However, it is sometimes difficult to calculate the local electronic structure to the necessary degree of accuracy. In this study, we verify the use of the combined PW and LO approach. As an example, we analyzed the hydrogen adsorption on a Pd(111) surface [1].

The concept of the combined PW and LO approach is illustrated in Fig. 1. The adsorption properties can be calculated as shown in Eq. (1).

$$E(\text{PW+LO, surface}) = E(\text{PW, surface}) - E(\text{PW, cluster}) + E(\text{PW, cluster}) \quad (1)$$

Figure 2 shows the potential energy surface of the hydrogen adsorption on the Pd(111) surface. We clearly demonstrated that the combined PW and LO approach is both effective and necessary to determine local surface phenomena. We expect that the proposed approach will be effective for a broad range of applications in the material science field.

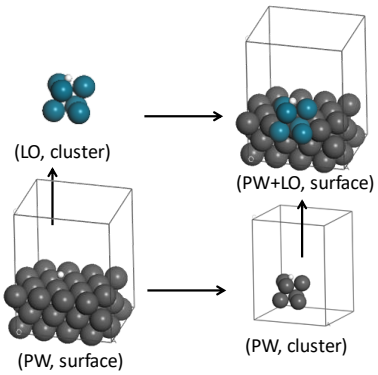

Figure 1. Concept illustration of the combined PW and LO approach.

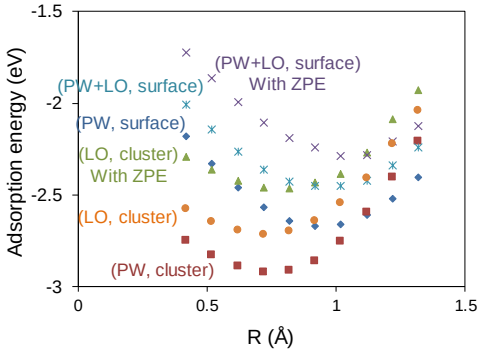

Figure 2. Potential energy surface of a hydrogen atom adsorption onto a fcc site on a Pd(111) surface.

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