What is the best density functional for adsorption?

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Underpinning virtually all machine learning investigations of surface processes are training data derived from density functional theory (DFT). With this, it is essential to ensure reliability of the chosen density functional approximation (DFA) and dispersion method for the domain under study. This is especially the case for surfaces due to opposing recommendations of DFAs for molecules versus solids. However, accuracy of DFAs for surface adsorption has only been quantified for a sparse set of adsorbate-surface combinations, and this task remains open for several modern DFAs which have shown great promise in other chemical domains. This work pulls together and evaluates several decades of high-accuracy calculations for surface adsorption, and evaluates relevant DFAs over this set. Among the best-performing DFAs are PBE-MBDNL, PBE-D4 and B86bPBE-XDM, with higher rungs of Jacob's ladder not displaying improved performance. Importantly, even for the best-performing DFAs, the mean error lies above the chemical accuracy threshold of 1 kcal/mol, and accuracy varies strongly between systems. Additionally, the performance of r^{2}SCAN and HSE06 is similar to that of PBE, indicating that these popular DFAs may not be worth the additional cost if targeting surface adsorption. This work highlights the limitations of DFT for surfaces and provides a strategy for choosing a suitable DFA among those currently available.

Figures

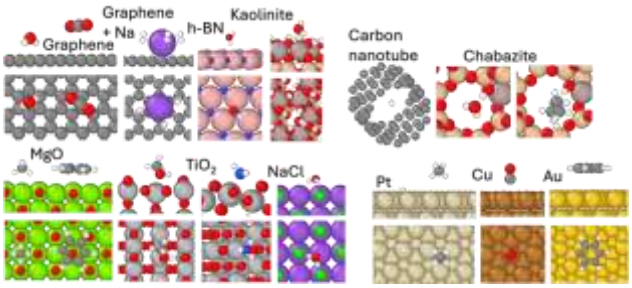

Figure 1. Schematic overview of a selection of the surfaces and adsorbates studied in this work.