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Non-reactive interaction of molecules with a surface: cluster or periodic approach?

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The non-reactive interactions of molecules with a metallic or ionic surface are subjects of numerous studies particularly for their importance in capture and release of molecules processes, in polarization of surfaces and also in energy transfers.

In such studies one has specifically to deal with long range interactions. With the usual periodic codes (VASP or Crystal), the surface is described by a periodic 2D-representation, namely a slab representation and the calculations are performed using Density Functional Theory (DFT) methods. In the physisorption domain, the weak interaction is governed by van der Waals (vdW) forces and it is well known that so far standard exchange-correlation functionals provide a poor description of such dispersion interactions [1] even though recent studies have shown that sophisticated DFT approaches can give promising outcomes for such difficult cases.

Alternative studies have been performed, modeling the metallic surface by a cluster as in recent theoretical calculations on the H_2/Cu or H_2/Ag systems using a cluster model consisting of 22 Cu or Ag atoms [Fig.1]. It has been shown that the chemisorption and physisorption of H_2 layers can be satisfactorily reproduced by highly correlated electronic wavefunctions (MRCI or CCSD(T) methods using MOLPRO[2]). Such pure ab initio methods are very efficient, they can provide reliable local properties (as for example rotational spectroscopy of the physisorbed molecule[3]) but they are missing delocalization effects, they are expensive and cannot be used for large systems.

In order to compensate the deficiencies of both, cluster and periodic approaches, the 22 atoms cluster has been included in a periodic frame, using the embedded method. This ansatz is shown to be helpful for short range interactions but cannot improve significantly the long range ones.

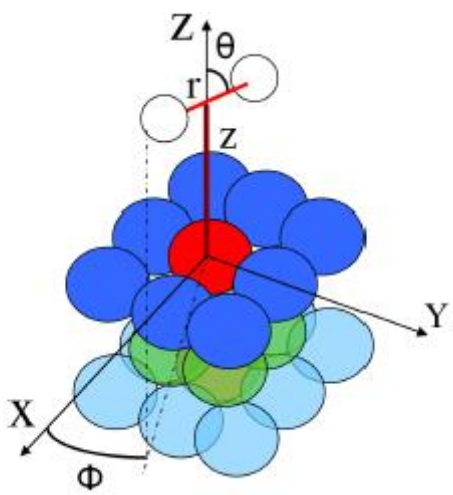

Fig.1 Representation of the H_2 Cu(22) cluster system.

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