Is DFT reliable for beryllium containing systems? The example of the Be – π system interaction

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Beryllium is known to be difficult to handle by the quantum chemistry methods currently available. The small 2s - 2p energy interval leads to quasi-degenerated electronic sates described by a multi-references wave function. In the gas phase, beryllium interacts through weak van der Waals (vdW) interactions as a consequence of its closed shell electronic configuration ($1s^2$ $2s^2$). In the bulk, it hybridizes and standard methods based on DFT and post-HF theory are given to be correct [1].

We herein investigate the ability of DFT based methods to describe the interaction between beryllium atom and graphitic systems. Recent DFT investigation [2] established that atomic beryllium is physisorbed on graphene while it chemically binds in a bilayer of graphite.

The critical case of the weak interaction that take place between an isolated beryllium atom and graphene is investigated at different level of theory: (i) density functional calculations with Grimme correction (ii) Single reference post Hartree-Fock methods: second-order Møller-Plesset (MP2) perturbation theory and coupled cluster method with the inclusion of single, double and perturbative triple excitations (CCSD(T)) (iii) Multi reference post Hartree-Fock methods: complete active space self consistent field (CAS-SCF) and complete active space with perturbation theory truncated at the 2nd order (CAS-PT2) (iv) Periodic density functional computations using the Perdew-Burke-Ernzerhof functional with the Grimme correction of the dispersion forces (PBE-D2).

The combined (i)-(iii) approaches allow us to select an accurate functional to describe the beryllium – graphene interaction (PBE-D2) and understand the electronic mechanisms that occur when beryllium interacts with the surface. Finally mechanisms of the beryllium - graphite interaction are understood and the validity of DFT based methods is established.

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[2] Ferro Y., Fernandez N., Allouche A., Linsmeier C., J. Phys. Condens Matter., 25:015002, 2013.