Embedding approaches for bulk systems using projector-augmented waves

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Density-functional embedding allows for combining different levels of theory in one calculation (for a review see [1]). Consider, for example, dissociative adsorption of gas molecules on metal surfaces: the extended metal surfaces can be accurately treated by periodic density functional theory approaches, while charge transfer processes at the adsorption site require more accurate correlated wave function (CW) approaches. The latter, in turn, scale unfavourably with system size, and thus do not allow for treating more than approximately fifteen heavy atoms. Instead, we separate the problem into a cluster of interest and the surrounding metal surface. Their interaction is mediated by a scalar embedding potential determined at the DFT level. The cluster can now efficiently be treated by CW techniques, in the presence of the embedding potential.

We have recently extended our approach [2] to the popular VASP software package, including the projector-augmented wave (PAW) formalism [3]. This allows for treating much larger unit cells at higher accuracy, and to exploit the full framework of VASP: the PAW formalism (i) offers an exact transformation between the original, oscillating wave function and the pseudized, slowly varying pseudo wave function used in the computation and (ii) explicitly treats the all-electron wave functions, albeit within the frozen-core approximation. We show that PAW-based density-functional embedding yields robust, accurate embedding potentials, and discuss application cases and future extensions based on a set of mutually orthogonal orbitals [4].

[1] F. Libisch, C. Huang, and E. A. Carter, Acc. Chem. Research, **47**, 2768 (2014).
[2] K. Yu, F. Libisch, and E. A. Carter, J. Chem. Phys. **143**, 102806 (2015).
[3] G. Kresse, and D. Joubert, Phys. Rev. B, **59**, 1758, (1999)
[4] F. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller Chem. Theory Comput., **8**, 2564–2568 (2012).