FHI-aims Cheat Sheet: Hybrid QM/MM calculations

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The use of periodic boundary conditions gives access to bulk or surface material properties. However, due to long range periodicity, this approach suffers from finite size effects when aperiodic systems such as defects, dopends, localized charges, or single molecule adsorption are to be simulated. This renders it necessary to apply very large supercells, which easily exceeds computational feasibility because of excessive memory demand.

For non-metallic materials there exists an hierarchical QM/MM approach, alternatively to the conventional periodic setup. In this approach, only the central region (QM-region) is treated on your quantum mechanical level of choice, while the remainder of the system (MM-region) is treated on a classical molecular mechanics level (see figure 1).

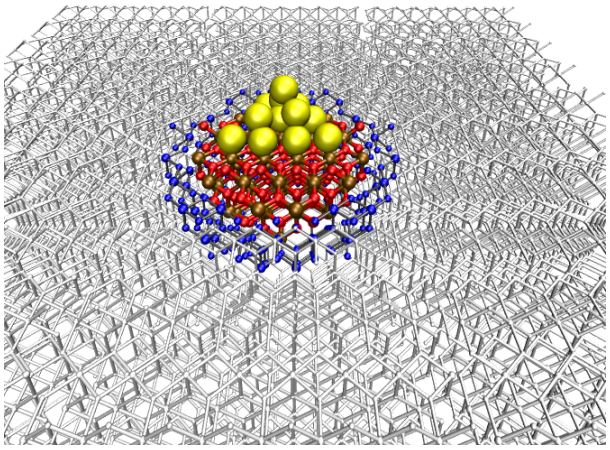

Figure 1: Example for QM/MM setup: $Au_n@TiO_2$. The adsorbed cluster and the direct vicinity of the substrate define the QM-region. The far-field surrounding (grey particles) pictures a monopole field with formal charges (4+ for Ti and 2- for O). In the blue region, oxygen particles are still represented as monopoles, while Ti-cations are described with ionic pseudopotentials.

The simplest setup for the MM-region is a field of monopoles. Using formal charges is a good choice in most cases. While interaction among MM particles is covered by appropriate force field parameters, coupling between QM and MM-region is purely electrostatic. However, positively charged monopoles act as Coulomb singularities for the explicit electrons in the QM-region, resulting in spurious charge leakage out of the QM-region. Replacing these monopoles by ionic pseudopotentials, wherever overlap between electronic wave-function and monopole

is possible, removes the Coulomb singularity and allow for chemically accurate (no dangling bonds) transition between QM and MM region.

If your are interested in a simple static electrostatic embedding, you can run QM/MM calculations stand-alone as a FHI-aims single-point calculation. More elaborate schemes are available via ChemShell[1] (see below).

How to begin?

FHI-aims needs following ingredients for a stand alone QM/MM calculation:

geometry.in: including positions of pseudocores and monopoles in the corresponding syntax (see figure 3).

control.in: needs to be augmented with a separate species (see figure 2) for pseudopotentials, including some specifications concerning the usage of the pseudopotential itself (see FHI-aims manual for the "full monty"). This pseudoized species **must not have any basis function**!

***.cpi** : pseudopotential file in the FHI98PP format.

```
[...]
  species        Ti_pseudo
#     global species definitions
    nucleus             22
    mass                47.867

    pseudo              Ti.cpi
    pp_charge           4.
    pp_local_component     1
    nonlinear_core      .false.

    include_min_basis .false.
[...]
```

Figure 2: Species data for a pseudoized titanium atom. Starting from the default species files only a few flags need to be added and the basis functions (accept the minimal basis) need to be removed.

FHI-aims expects the pseudopotentials in the standard format of FHI98PP[2] (*.cpi) and to be present in the same folder as the control.in. As these are fully-separable nonlocal pseudopotential following the recipe of Kleinman-Bylander [3], one needs to specify the local component and switch on/off nonlinear core correction. An almost complete library of *.cpi files can be found on http://www.abinit.org/downloads/psp-links.

Alterantively:

For dynamic solid state embedding it might be convenient to make use of the ChemShell interface[1]. It connects FHI-aims to a number of molecular mechanics package to allow for self-consistent polarization of the MM-region, geometry optimization or simple dynamics: FHI-aims calculates coupling force terms between QM and MM particles; the molecular mechanics package propagates the particles and and updated updated geometry.in file is generated

```
pseudocore  x   y   z   species

multipole   x   y   z   0   charge
```

Figure 3: Geometry in style-guide for a embedded QM/MM setup. The species of the pseudopotential need to correspond with the species specified in control.in.

for the next FHI-aims iteration. Besides that, it provides several helpful routines for cutting the QM region and fitting additional monopoles to reproduce the long-range periodic electrostatics of a infinite crystal [4]. The key ingredients are the systems geometry parameters (periodic supercell), force field parameters for pairwise interaction between embedding monopoles and their polarizability and finally a pseudopotential for cations in the transition zone. ChemShell will periodically reproduce the supercell, hierarchically divide the system into QM and MM region, and generate geometry input for FHI-aims. Find more information on http://www.cse.scitech.ac.uk/ccg/software/chemshell/manual/.

Attention!

These cheat sheets are not intended to substitute for reading the manuals of the programs involved and the original literature cited therein!
Have fun!

References

[1] Paul Sherwood et al. Quasi: A general purpose implementation of the qm/mm approach and its application to problems in catalysis. *Journal of Molecular Structure: THEOCHEM*, 632(1-3):1 – 28, 2003.

[2] Martin Fuchs and Matthias Scheffler. Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density-functional theory. *Computer Physics Communications*, 119(1):67 – 98, 1999.

[3] Leonard Kleinman and D. M. Bylander. Efficacious form for model pseudopotentials. *Phys. Rev. Lett.*, 48(20):1425–1428, May 1982.

[4] Alexey A. Sokol, Stefan T. Bromley, Samuel A. French, C. Richard A. Catlow, and Paul Sherwood. Hybrid qm/mm embedding approach for the treatment of localized surface states in ionic materials. *International Journal of Quantum Chemistry*, 99(5):695–712, 2004.