MAPS

Application Note

Treating dispersion effects in extended systems by hybrid MP2: DFT with QmPot

Modules used
MAPS
QmPot
Turbomole
ABINIT

The increasing demand for computational resources with increasing size of a chemical system is the major factor that hampers the application of ab initio methods to condensed phase and surface problems.

Prominent examples of the latter are the determination of active site structures as well as the prediction of free energies and rates for elementary steps in enzymatic and heterogeneous catalysis. One possible solution of the problem is to limit the quantum mechanical (QM) treatment to the "active part" of the system, and to describe its environments by simple parameterized interatomic potential functions.

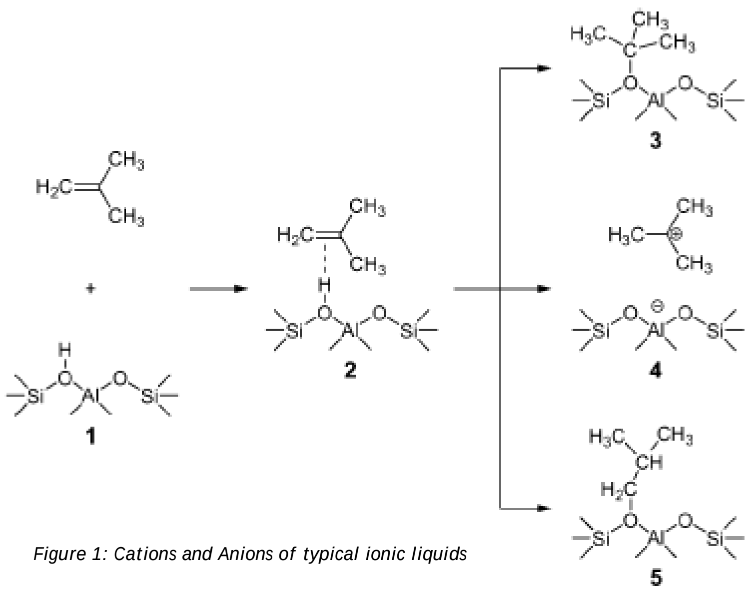

Figure 1: Cations and Anions of typical ionic liquids

Nowadays, such approaches are very popular and known as hybrid quantum mechanics molecular mechanics (QM/MM) methods. The term "molecular mechanics" stresses the force field type of interatomic potential function.

However, there are other situations in which we need to have a computational scheme that allows to go beyond the current capabilities of established computational methods.

For instance, Density functional theory (DFT) has become the most popular method in computational chemistry, but it was also realized that widely used functionals do not properly account for dispersion interactions. Dispersion is known to be a key quantity for the type of reactions discuss in this application note (see Figure 1).

Indeed, dispersion is an intermolecular electron correlation effect, and the simplest quantum mechanical (QM) method for electron correlation, second-order Møller–Plesset perturbation theory (MP2), describes dispersion well. MP2 calculations, however, are far more expensive than DFT calculations and there is no any periodic implementation of such method. Here the use of a hybrid QM: QM method through QmPot integrated in MAPS, combining MP2 calculations for the reaction site C with DFT calculations for a large extended system S under periodic boundary conditions is presented. The example of a hydrocarbon transformation in a pore of a zeolite is considered.

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The energy of the periodic system S is obtained by:

$$E_{hybrid} = E(S)_{low} + E(C)_{high} - E(C)_{low}$$

The integration of QmPot in MAPS allows the access to several tools that enable the easy selection of a cluster as well as the setup of the calculation. QmPot in general allows the combination of the following "low level" engines: LAMMPS, MNDO, Abinit with the "high level" ones: Turbomole and MNDO.

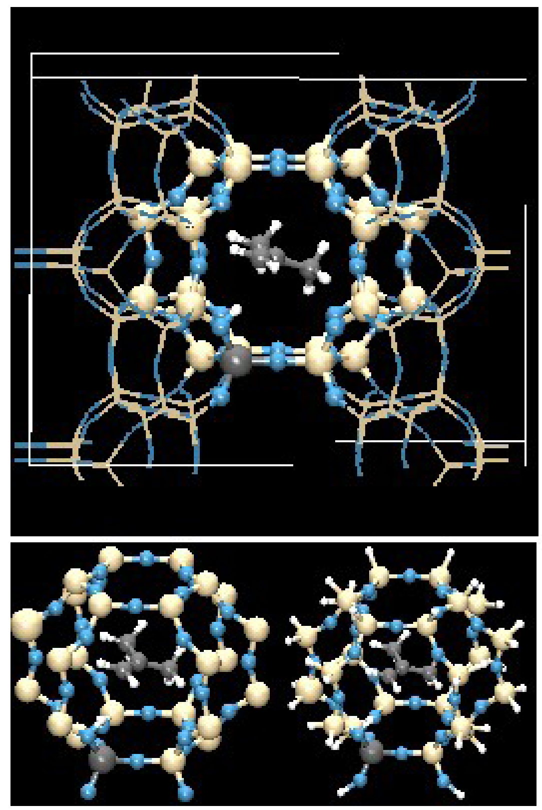

Figure 2: (top) the cluster C visualized within the full system S. (bottom left) the cluster isolated and (bottom right) the cluster with the Link Atoms used in QmPot.

In the particular case examined here the use of QmPot provides the following insight:

- Different structural parameters (correcting DFT over-binding)
- Structures 2 and 5 are the most stable
- Smaller relative stability of carbenium (structure 4) (PBE overestimates electrostatic attraction between weakly bounded fragments)

The table below lists a comparison of the relative energetic positioning of the structures presented in Table 5 (see below)

Table 5 Final estimates of periodic MP2 reaction energies for the formation of structures 2–5 from 1 and isobutene. Numbers are given in kJ mol^{-1}

	2	3	4	5
MP2:PBE result[a]	−77	−66	−13	−80
CBS limit correction[b]	15	40	18	33
Periodic model correction[c]	−16	−22	−26	−26
Estimate periodic MP2	−78	−48	−21	−73
(Difference to PBE[d])	(−62)	(−67)	(−29)	(−70)

[a] Not corrected for the BSSE (see Table 2). [b] $\Delta E(C)_{MP2}$ term (see Table 3). [c] $\Delta E(C)_{MP2} - \Delta E(C)_{PBE}$ term (see Table 4, aug(O)-TZVPP basis set). [d] Periodic DFT (PBE) structure optimisation (see Table 1).

Reference

Sauer et al.Phys. Chem. Chem. Phys., 2006, 8, 3955–3965.

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