BREQM: Boundary Region Embedding Quantum Mechanics/Molecular Mechanics

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Abstract

Quantum Mechanics/Molecular Mechanics (QM/MM) atomic-scale simulations can efficiently describe large systems with high accuracy. QM/MM accomplishes this feat by only treating small regions of interest with QM; less-important regions are described with classical MM. Conventionally, interactions between QM and MM regions are accounted for using force fields. However, since accurate reactive force fields are difficult to develop, we propose a new methodology: boundary region embedding QM/MM (BREQM). In BREQM, we introduce a boundary region through which the QM and MM regions can influence one another. Compared to conventional QM/MM, BREQM can more easily and consistently model heterogeneous catalysts, which are of great industrial and technological importance.

1 Motivation

Quantum Mechanics/Molecular Mechanics (QM/MM) allows accurate computational simulation of systems containing thousands of atoms. It achieves this feat by limited QM treatment to the most important part of a system while treating the remainder of the system with classical MM. Indeed, QM/MM is useful when simulating systems consisting of a small reaction center surrounded by solvent, such as proteins and heterogeneous catalysts.

When applying QM/MM to heterogeneous catalysts, the choice of QM region is fairly obvious (figure 1). The catalyst atoms and nearby solvent molecules should be modeled using QM, since these atoms participate in surface chemistry. Although the bulk-like solvent further away from the catalyst surface does not directly influence surface chemistry, it is nevertheless an important part of the system. Therefore, the bulk solvent should be included in the MM region.

Density functional theory (DFT) and force fields can easily describe QM and MM regions. The challenge in QM/MM simulations is to describe the important interactions between atoms in the QM region ("QM atoms") and those in the MM region ("MM atoms"). The simplest, conventional approach is *mechanical embedding*, in which a force field is used to describe these interactions.

We see two issues with using conventional mechanical embedding to study heterogeneous catalysis:
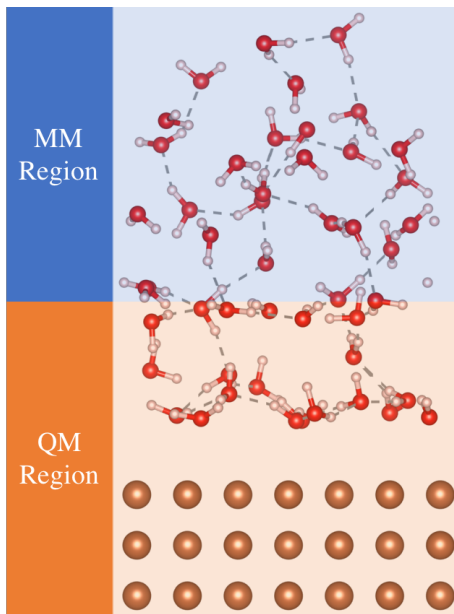

Figure 1: Side view of a periodic QM/MM model of the Cu(100)/water system. Solvent near the Cu slab forms layers due to Cu/water interactions and therefore should be included in the QM region. Further from the surface, bulk solvent should be part of the MM region.
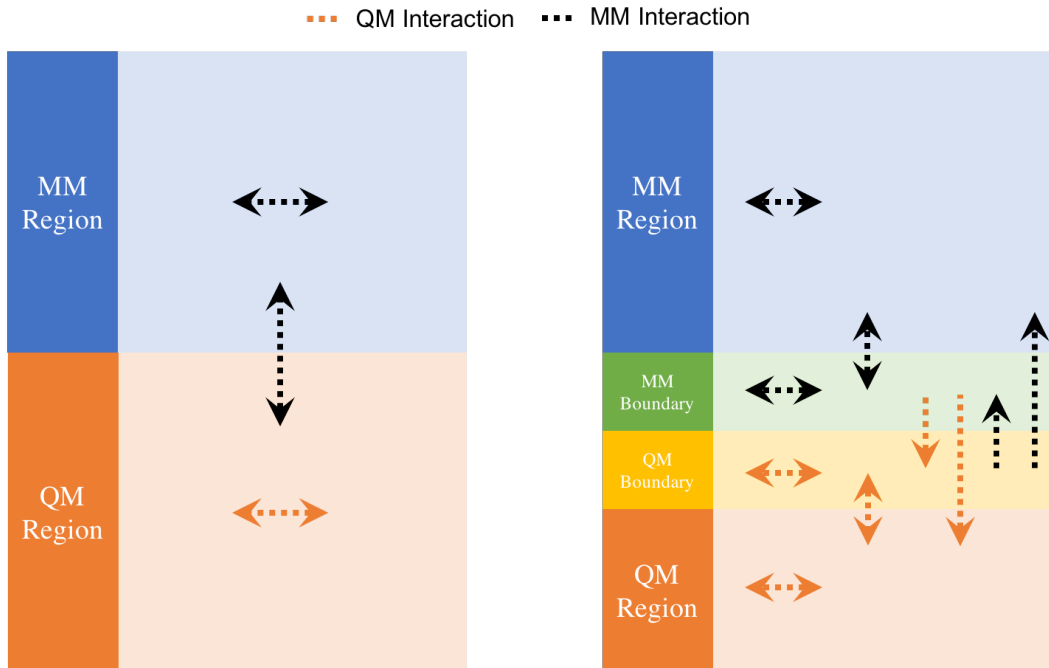
Figure 2: Interaction diagram for mechanical embedding (left) versus boundary region embedding (right). Arrows indicate directional influence of interactions.

- **Issue 1.** For complex catalysts, such as multimetal oxides, developing the required reactive force fields is prohibitively time-consuming and difficult. This limits applicability of mechanical embedding QM/MM to simple metal catalysts.

- **Issue 2.** Mechanical embedding QM/MM is, on a fundamental level, inconsistent. MM-derived forces can heavily influence QM atoms. We would prefer cleaner separation between the QM and MM regions, with solely QM-derived forces influencing QM atoms.

These two issues motivate our development of boundary region embedding QM/MM (BREQM), whose methodology and implementation are described in the following sections.

2   Methodology

We introduce two boundary regions which separate the QM and MM regions. In this paper, we consider the *QM part* of the system to consist of the QM region and the QM boundary. Likewise, we consider the *MM part* of the system as the MM region and the MM boundary. *MM atoms* are those contained in the MM part, while *QM atoms* are those contained in the QM part. The interactions considered by mechanical em-

bedding QM/MM versus BREQM are diagrammed in figure 2:

- In BREQM, we neglect interactions between the QM and MM regions. If the QM region is chosen to enclose the catalyst, this means that using BREQM only requires a reactive force field for the solvent. In this way, we resolve issue 1.

- Using boundaries, we cleanly separate the QM and MM parts of the system. We ensure that QM atoms are only influenced by QM-derived forces, while MM atoms are only influenced by MM-derived forces, resolving issue 2.

3   Implementation

We implemented BREQM in Python. To calculate QM (DFT) forces, the code interfaces with Vienna Ab initio Simulation Package (VASP) [1-4]. To calculate MM (force field) forces, the code interfaces with the LAMMPS molecular dynamics simulator [5]. Within LAMMPS, many force fields can be used, most notably the ReaxFF reactive force field [6].

The user provides an input structure and specifies BREQM regions. The user also provides input parameters for VASP and LAMMPS calculations, giv-
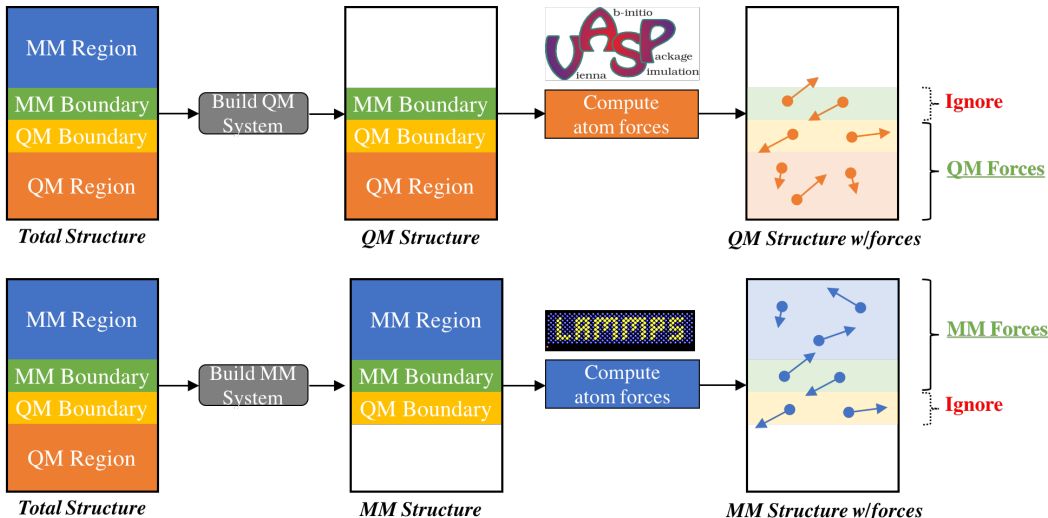
Figure 3: Basic processes for calculating MM forces (top) and QM forces (bottom) using LAMMPS and VASP. Combining the QM and MM forces, we can capture the BREQM interactions diagrammed in figure 2.

ing the user complete control over the QM and MM calculations.

As diagrammed in figure 3, the code first splits the input structure into QM and MM structures as specified by the user. These structures are sent to VASP and LAMMPS, respectively, which compute various forces. The code than extracts the relevant forces from each software package's output to capture the BREQM interactions as defined in figure 2. This process is elaborated in figure 3.

By using this process to calculate QM and MM forces, the python code can perform velocity-verlet molecular dynamics (MD), in effect simulating the system with energy fixed (NVT ensemble). By scaling velocities (according to a Maxwell-Boltzmann distribution), the code controls the system's temperature. The user can use velocity rescaling to steadily heat/cool the system or hold the system around a certain temperature.

3.1   Bond Breaking

In QM/MM simulations, bonds can potentially be broken when splitting the system into QM and MM structures. Within the BREQM methodology, bonds can break between the QM region and QM boundary and between the MM region and MM boundary (see figure 3). Bond breaking can have disastrous consequences, since it leads to incorrect QM-computed wavefunctions and MM-computed atomic charges, both of which are central to force calculations.

We developed BREQM with heterogeneous catalysis in mind, so we easily sidestepped the problem of bond breaking. We did this by ensuring that the QM region/QM boundary and MM region/MM boundary interfaces are contained within the solvent. Since the solvent is composed of small, individual molecules, we use automatically calculated bonding information to ensure that solvent molecules are never broken.

3.2   Incompatible Timesteps

Since MM-derived forces are less accurate then QM-derived forces, MM MD requires smaller timesteps than QM MD. For example, ReaxFF force field MD works best with a 0.25 fs timestep while DFT MD can tolerate a timestep as large as 1.00 fs.

To account for different timesteps, we developed a simple QM/MM MD scheme diagrammed in figure 4. Rather than perform each MD step on the entire system, we separately perform MD steps on the QM and MM parts of the system and then merge the structures together. The QM and MM parts of the system are technically out of phase by a single QM timestep. However, since simulations are performed over hundreds of timesteps, this is inconsequential.

4   Conclusion

We implemented an alternative to mechanical embedding QM/MM which we call boundary region embedding QM/MM (BREQM). By capturing interaction between QM and MM regions using two
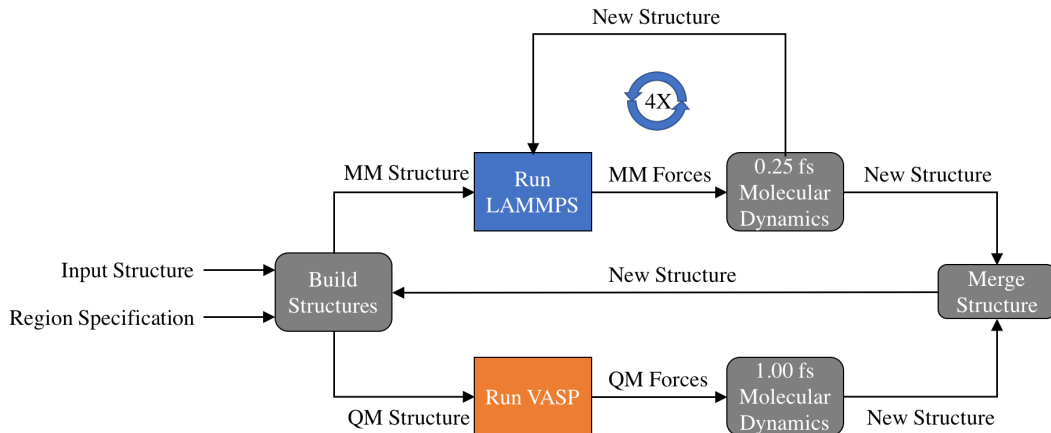
Figure 4: QM/MM MD scheme using a MM timestep 4x smaller than the QM timestep.

boundary regions, we can more simply and consistently apply QM/MM molecular dynamics to simulate complex heterogeneous catalysts. We hope to use BREQM to carry out molecular dynamics (MD) runs on the order of hundreds of picoseconds in order to observe and study catalytic mechanisms.

We wrote Python code which orchestrates BREQM and interfaces with the VASP and LAMMPS software. Within the code, we implemented NVE MD. Next, we will implement NVT MD.

With NVE and NVT molecular dynamics implemented, we will study the oxygen reduction reaction on the Pt(111) surface. This reaction is central to to the operation of hydrogen fuel cells. In the course of this study, we will have a chance to critically evaluate BREQM and develop best-practices when applying BREQM, all while increasing our understanding of this important catalytic process.

5 References

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