A multi-scale code for flexible hybrid simulations

L. Leukkunen¹, T. Verho² and O. Lopez-Acevedo¹

¹COMP Centre of Excellence, Department of Applied Physics, Aalto University, P.O. Box 11100, 00076 Aalto, Finland ²Molecular Materials, Department of Applied Physics, Aalto University,

P.O. Box 11100, 00076 Aalto, Finland

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Abstract

Multi-scale computer simulations combine the computationally efficient classical algorithms with more expensive but also more accurate ab-initio quantum mechanical algorithms. This work describes one implementation of multi-scale computations using the Atomistic Simulation Environment (ASE). This implementation can mix classical codes like LAMMPS and the Density Functional Theory-based GPAW. Any combination of codes linked via the ASE interface however can be mixed. We also introduce a framework to easily add classical force fields calculators for ASE using LAMMPS, which also allows harnessing the full performance of classical-only molecular dynamics. Our work makes it possible to combine different simulation codes, quantum mechanical or classical, with great ease and minimal coding effort.

1 Introduction

1.1 Multiscale Computations

Computer simulations are a valuable tool in modern molecular physics research. They can provide insight into dynamics of a complex system which can be hard to attain through actual experimentation and they are able to deliver results in scenarios that can be hopelessly beyond capabilities of current analytical methods.

Despite its significant potential, computational physics faces challenges in practice arising from the computational cost associated with many high precision algorithms. This leads to continuous balancing of the desire for accuracy with the cost of reaching it. There is a large performance gap between ab initio DFT algorithms and the computationally cheap but quite system specific classical force field algorithms. This has created a need for a mechanism that would allow bridging this chasm in order to simulate systems with thousands of atoms while retaining the flexibility of modeling quantum mechanical behavior that arises, without having to first spend significant effort in tuning the classical force fields to work in the particular system under scrutiny.

There can be considered to be two main approaches to a solution to this. First method attempts to develop and improve fast classical methods to incorporate behavior arising from quantum mechanical features. Reactive force fields are one such example of this class of solutions. The second path is the attempt to combine two or more algorithms into a single uniform multi-scale simulation. An example of this approach is ONIOM [10] developed by Gaussian. Both approaches have their strengths and weaknesses and currently no universal answer exists. Multi-scale setups tend to lead to problems at the interface region between the calculation methods, while reactive force fields face difficulties coping with systems that fall outside the setups for which they were trained for.

1.2 Atomistic Simulation Environment

Atomistic Simulation Environment (ASE)[2] is an open source software framework designed to perform simulations using a number of algorithm implementations. These algorithms are called calculators in ASE. The calculator interface is defined so that an adhering class must provide functions that calculate both forces acting on the atoms and the total potential energy of the system. ASE itself is written in Python programming language, but the actual calculator implementation can be something else, as long as a Python class wrapping the implementation is provided.

The force and energy information provided by the calculators is used by various other ASE modules to perform a range of molecular dynamics operations. These include structure relaxation along with constant NVE/NVT molecular dynamics. Structure relaxation is also considered a molecular dynamics operation even if there is no time progression involved.

Using ASE consists typically of writing small Python scripts that create the atom configuration and setup the calculators and any molecular dynamics operations that are to be performed. The framework is designed so that the central object is the Atoms class, which stores all the arrays describing the atoms of the system. The calculator is then assigned to this Atoms object, essentially resulting in a one to one mapping. At present the ASE framework does not provide any facilities for combining multiple calculators into a single simulation.

1.3 GPAW

GPAW [4] is a projector-augmented wave (PAW) [3] implementation designed to work with ASE. PAW takes account of the core electrons of atoms as frozen, and computes with soft pseudo valence wave functions. GPAW supports all the exchange-correlation functionals provided by the libxc library [6]. While GPAW reaches good accuracy, it is compute intensive, requiring large cluster computers to simulate systems larger than just tens of atoms. For GPAW a huge simulation is already something with 500 atoms and for that kind of calculation

a cluster with thousands of nodes is needed in order to produce results in a reasonable amount of time.

1.4 LAMMPS/ReaxFF

LAMMPS [7] is a classical molecular dynamics simulator. It is a mature framework that supports parallel distributed memory cluster computers. Similar to ASE, it allows different algorithms to be plugged in through an extension mechanism. One such algorithm is the ReaxFF [8] developed by Adri van Duin. ReaxFF has been developed to bridge the gap between ab initio quantum mechanical algorithms, such as GPAW, and the existing empirical force field (EFF) methods. Unlike traditional EFF methods, ReaxFF is capable of describing reactive systems. As is the nature of LAMMPS as a simulation environment, ReaxFF produces potentials describing the interactions of atoms. These are trained using ab initio techniques to fit a particular system, but unlike some EFF algorithms, there is only one version of each atom type used in a single simulation.

The performance difference between LAMMPS/ReaxFF and ASE/GPAW is significant. In a simulation of a system containing 5000 atoms of which 10 are computed using GPAW, the ReaxFF computations take so little time it is not worth to even consider parallelizing that part as the GPAW computation of its tiny subset of atoms completely dominates CPU usage.

2 ASE/LAMMPS interface

2.1 Design of the interface

Since the standard ASE distribution merely offers rudimentary support for LAMMPS that only allows nonbonded interaction, we took upon ourselves to improve the interface. Because LAMMPS supports a large number of functional forms for force fields, a great many force fields can be used through LAMMPS. Therefore, in our design, each LAMMPS force field is a separate calculator class in ASE. However, all of them inherit a base class for LAMMPS calculators, LAMMPSBase, that handles all communication with LAMMPS. The responsibility of the subclasses is to (a) provide the force field parameters as a FFData object, (b) handle atom typing, i.e. determine a force field specific type for each atom, depending on its chemical environment, and (c) possibly assign partial charges to atoms for calculating electrostatic interactions. The methods in LAMMPSBase then detect chemical bonds, bond angles, dihedrals and improper dihedrals in the system and generate LAMMPS input based on the force field parameters provided by the subclass.

The main steps for adding support for a new LAMMPS force field consist typically of writing a parser that reads a force parameter file acquired from an external source, and enabling automatic atom typing for the force field. To make automatic typing as easy as possible, we defined a template syntax for defining chemical environments that characterize a given type. For each type, a template expression consisting of a single line is given, and to avoid ambiguity with multiple matching types, precedence expressions for defining priority among types can be used.

In order to offer maximal performance in molecular dynamics simulations that do not involve mixing with quantum mechanical calculators, we wrote ASE dynamics classes that are specific to the LAMMPS calculators. Their purpose is to allow running dynamics inside LAMMPS without needing to execute Python code between every timestep. The syntax for using these LAMMPS dynamics classes is identical to that when using the standard ASE dynamics classes, but instead of executing the LAMMPS calculator timestep by timestep, they instruct the calculator to execute LAMMPS molecular dynamics runs with given parameters. The run is divided into shorter runs in order to save ASE trajectory snapshots along the way, also allowing the use of "observer" functions in the same way as the standard ASE dynamics classes. In the future, the concept of LAMMPS specific dynamics classes can be used to expose the rich feature set of LAMMPS to the ASE user in a clean way. This could include robust equilibration methods such as replica exchange dynamics.

Even though the present paper is geared towards mixing the LAMMPS calculator with quantum codes, we regard the interface potentially useful for purely classical molecular dynamics simulations as well. In addition to allowing running LAMMPS from ASE, it automatizes many task such as atom typing and generating LAMMPS input parameters, something that the LAMMPS native interface leaves to the user.

2.2 Using the interface

We illustrate the usage of the LAMMPS interface with a simple molecular dynamics involving a phenol dimer. The initial geometry is obtained from the s22 data set included in ASE, and we demonstrate two different LAMMPS calculators, ReaxFF and CHARMM general force field for drug-like molecules[9]. The code in listing 1 runs a 10 picoseconds simulation with first ReaxFF and then CHARMM, and saves the trajectories in two separate files.

```
from ase.data import s22
from ase import units
from multiasecalc.lammps import ReaxFF, CHARMM
from multiasecalc.lammps.dynamics import LAMMPS.NVT
from multiasecalc.utils import get_datafile
atoms = s22.create_s22_system('Phenol_dimer')
atoms.calc = ReaxFF(get_datafile('ffield.reax'))
dyn = LAMMPS.NVT(atoms, 1*units.fs, 300, trajectory='reax.traj')
dyn.run(10000)
atoms.calc = CHARMM(get_datafile('par_all36_cgenff.prm'))
dyn = LAMMPS.NVT(atoms, 1*units.fs, 300, trajectory='charmm.traj')
dyn.run(10000)
```

Listing 1: Molecular dynamics with LAMMPS

As an aside, we don't implement any partial charge determination scheme in the CHARMM force field, so the user needs to apply a suitable charge equilibration method prior to simulation. In listing 1, we use the build-in charge equilibration algorithm in ReaxFF to provide partial charges for the CHARMM simulation.

3 Force and Energy Mixer

3.1 Design of The Mixer

The easiest way to combine results from two calculators is to simply assign different atoms to each and then present the combined results. This is guaranteed to produce errors as the interaction between the two sets of atoms is not taken into account at all.

To avoid this error, the Mixer employs a strategy based on ONIOM, a method developed by Gaussian. The basic idea is to calculate the full system using the cheap less accurate algorithm, then correct this result by adding the result from calculating the quantum mechanically interesting sub-system with the QM method. At this point the QM sub-system atoms are calculated twice, so a further correction is done by removing the same QM subsystem calculated using the classical method.

This still leaves something to be desired, as the outer edges of the QM sub-system will have substantial errors introduced in the calculations due to the arbitrary system boundary. To avoid this, the Mixer uses weights that can be assigned to atoms for each calculation, controlling how big contribution it will make to the final result. The weights can either be fixed to each atom permanently, or calculated dynamically depending for example on the position of the atom.

It is important to keep in mind that the Mixer itself imposes very few restrictions on how the forces and energies of the sub-calculators are combined. It can support any number of calculators, used in any number of force and energy calculations, with atoms and their weights and coefficients set separately for each and updated dynamically as the simulation progresses. In this work we primarily concentrate on a setup where two calculators are used but this in no way implies that the Mixer could not be used in a more creative way.

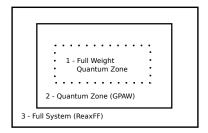


Figure 1: Simple 2D Calculation Region Arrangement

For a concrete example, we can consider the simple two calculator configuration shown in figure 1 and have the outer box 3 simulated using a classical method and a smaller inner box 1 using a QM method. For energies we are somewhat restricted by how the potential energy is calculated. The ASE calculators only provide a single potential energy value for the full system they computed, there is no way to split that up into finer components in a general way. We will therefore stick to the basic ONIOM Hamiltonian:

$$H = H_{3C} + \{H_{2Q} - H_{2C}\}.$$
(1)

Forces are given on a per atom basis by ASE calculators, so we have more flexibility in calculating the mixed combination. The equation for forces acting on atom i is:

$$F^{i} = F^{i}_{3C} + w^{i}(F^{i}_{2Q} - F^{i}_{2C}).$$
⁽²⁾

The numbers 1, 2, 3 refer to the regions of space so that 1 is the fully quantum inner box, 2 the inner box + transition region and 3 the full system. Letters Q and C refer to the calculators used: Q for quantum and C for classical.

This leaves us with a slight discrepancy between the force and energy calculations but the additional error dampening given by the weights for forces could help achieve for example better relaxation results. The Mixer design allows the user to control the weight configuration entirely, affording complete tailoring of these aspects of the calculation to the problem at hand.

3.2 Implementation of The Mixer

The Mixer is designed to present two or more ASE calculators as one towards the rest of the ASE framework. This is achieved by making the mixer appear as an ordinary ASE calculator itself. It provides a single set of forces and a single total potential energy for the given Atoms object. It can therefore take part in all the molecular dynamics operations ASE supports.

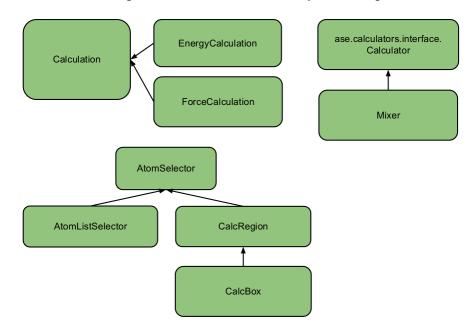


Figure 2: Mixer Class Diagram

As the Mixer inherits from the ASE interface class for calculators, it meets the requirements for a normal ASE calculator. It then further extends this functionality by providing a set of constructor parameters and member methods for registering a set of force and energy calculations. The main role of the Mixer class is to simply sum up the contributions from the sub-calculations using the coefficients given by them. The coefficients are primarily used to control the sign of the contribution. Almost all actual complexity of the Mixer concept is separated out to the Calculation and AtomSelector classes. This has been done to allow the user to completely control the way the multi-scale calculations are to be combined without having to modify the Mixer implementation itself.

The Mixer Calculation classes have an ASE calculator and an AtomSelector assigned to them. The AtomSelector is used to select the correct atoms from the original full system Atoms object. Two implementations of this selector functionality are provided. First is AtomListSelector, which filters based on an atom ID list, and second is the CalcBox, which selects atoms that fall within its extents. These demonstrate the flexibility provided by the Mixer design and can be used as a model for how the user can implement custom atom selectors to meet requirements of a particular simulation. The AtomSelectors are also responsible for providing the weight used in ForceCalculations. This means there are two separate factors affecting the computation of forces. The first is the weight that AtomSelector assigns, and second is the coefficient provided by the ForceCalculation. This may seem slightly strange at first, but this design allows re-using the same AtomSelector in multiple ForceCalculations. Looking at equation (2) it can be seen that in that scenario the same weight is used with both a positive and a negative sign.

Testing is an important part of developing a simulation tool. Unit tests have been written for all the main functionality of the Mixer. Specifically the CalcBox weight generation and molecule entry/exit have been tested carefully. Many of the classes support a debug level that can be specified in the constructors. Debug output is written into a human readable textfile.

3.3 Using The Mixer

In this section we examine how the Mixer is used in practice. We prepare a simple multi-scale simulation with just two hydrogen atoms. The code snippets demonstrate the procedure in a more tangible form.

There are four parts necessary for a Mixer calculation. First a valid ASE Atoms object must be created, the second component is a set of ASE calculator objects, third are the force and energy Mixer calculations and finally the fourth and final piece are the AtomSelector objects that are used to carve the Atoms object to parts given to each calculation.

The Atoms object can be created in the normal ASE way. Typically it is created by a separate script that stores it in an ASE Trajectory file and read into the actual calculation script later. Mixer places no restrictions to the contents of the Atoms object. The only special preparation that needs to be performed is executing Mixer.set_atom_ids(atoms) method, which adds a new Atoms-internal array to the atoms object, containing unique integer identifiers to each atom.

```
Mixer.set_atom_ids(atoms)
```

Listing 2: Declare Atoms object

This part is in accordance to the way Atoms class is designed to work, so it does not interfere with any existing ASE functionality and is automatically handled correctly by the various splicing and extending methods of the Atoms class. These unique identifiers are critical for correctly combining forces provided by the sub-calculators.

After preparing the Atoms object with the unique IDs, the user can proceed to creating instances of the ASE calculators to be used by the Mixer.

Listing 3: Create ASE calculators

In this simulation we want one of the hydrogen atoms to be in the classical region, and the other in the quantum region. This is obviously quite unphysical and the results are not very useful, but does serve well as a straightforward example. We proceed by creating two selectors to split the atoms into these two regions.

Listing 4: AtomSelector objects

The atom ids that the selector will select for are 0, 1 for the full system, and 1 for the QM region. The second parameter to the constructor is the set of weights assigned to each atom.

Now we are ready to define the Calculation objects for this system. Since we are going to implement, at least in principle, the calculations based on equations (2) and (1), we need six calculation objects. Three for energies and three for forces. This may look a little verbose, but considering the flexibility this allows, the trade off is worth it.

```
forces_qm_region_reaxff = ForceCalculation ("forces_qm_reaxff",
                                            qm_region)
forces_qm_region_reaxff.calculator = reaxff_calc
forces_qm_region_reaxff.cell = (60.0, 60.0, 60.0)
forces_qm_region_reaxff.coeff = -1.0
energy_full_system_reaxff = EnergyCalculation("energy_full",
                                               full_system)
energy_full_system_reaxff.calculator = reaxff_calc
energy_full_system_reaxff.cell = (60.0, 60.0, 60.0)
energy_qm_region_reaxff = EnergyCalculation ("energy_qm_reaxff",
                                             qm_region)
energy_qm_region_reaxff.calculator = reaxff_calc
energy_qm_region_reaxff.cell = (60.0, 60.0, 60.0)
energy_qm_region_reaxff.coeff = -1.0
energy_qm_region_gpaw = EnergyCalculation("energy_qm_gpaw",
                                           qm_region)
energy_qm_region_gpaw.calculator = gpaw_calc
energy_qm_region_gpaw.cell = (6.0, 6.0, 6.0)
```

Listing 5: Calculation objects

Now all that is left is creating the Mixer calculator object and running the simulation. The Mixer constructor takes two lists that comprise the sets of force and energy calculations.

Listing 6: Mixer instance creation

From this point onwards the atoms object can be used in exactly the same way as usual in ASE. All calculations will happen transparently in the background.

3.4 Mixer Unit Tests

A rudimentary unit test set has been developed. The tests have been built using the Python unittest class. Main focus is on the AtomSelectors and the supporting OctreeNode. The tests exercise the classes in isolation to make the results easier to interpret.

For OctreeNode the tests create and populate a volume and test finding these objects using various search radius. This mimics the way CalcRegion atom selector uses OctreeNode. AtomSelector tests focus on the CalcBox class as CalcRegion and the underlying Atom-Selector functionality gets completely and predictably covered that way too. Transition region weight generation is a key functionality and is extensively tested. Furthermore, the computations demonstrated in section 4 have been encapsulated into test cases as well.

For the CalcBox class we have developed a separate mixer_box.py Python script that can be used to run a two calculator computation as described by equations (1), (2) and figure 1. This script has been used during development for ad-hoc testing, but it is of sufficient quality to be used by users. It takes a number of command line parameters that control its behavior including specification of ASE trajectory file for input, the dimensions of the calculation regions and choosing the molecular dynamics to use and the number of steps to run among other variables. It also serves as a complete example of how the Mixer framework can be utilized to construct computation schemes for multiscale calculations.

4 Simple molecular systems in hybrid simulations

4.1 Interaction energy

To demonstrate the use of the LAMMPS interface and the Mixer using the implemented framework [1] we calculate the interaction energy of a 2-pyridoxine 2-aminopyridine complex shown in figure 3. The equation for interaction energy of the dimer is

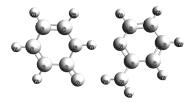


Figure 3: 2-pyridoxine 2-aminopyridine complex

$$H_{interaction} = H_{total} - H_{2-pyridoxine} - H_{2-aminopyridine}.$$
(3)

In the Mixer calculations we treat the molecule on the left (2-pyridoxine) using GPAW and the full system using LAMMPS/ReaxFF. In table 1 are presented the molecular and interaction energies computed first using ReaxFF and GPAW alone, and then together through Mixer. The Mixer calculations have been performed to match the energy equation (1) and in code look very similar to what is found in listings 2 through 6.

The interaction energies found in table 1 differ somewhat from the value -0.72eV published in [5], but this is expected as that value has been achieved using coupled-cluster method, and these here are of lesser accuracy by design.

4.2 Forces

In order to verify the force mixing functionality of the Mixer, a system consisting of a methane molecule is used. The molecule is moved along the x-axis so that it passes through the central

| Energy | ReaxFF | GPAW/PBE | Mixer (GPAW + ReaxFF) |
|-----------------|-------------|-------------|-----------------------|
| 2-pyridoxine | -62.339058 | -78.485885 | -78.519775 |
| 2-aminopyridine | -66.263778 | -83.629371 | -66.263778 |
| Combined | -128.974632 | -162.745084 | -145.155333 |
| Interaction | -0.371795 | -0.629827 | -0.371780 |

Table 1: 2-pyridoxine 2-aminopyridine energies

region of the simulation box. This motion on the x-axis is the only time integration done on the system, the relative positions of atoms remain constant to make comparison of forces calculated in different molecule positions easier. The computations are configured similar to what is shown in figure 1 but expanded to three dimensions.

LAMMPS/ReaxFF is used to model the full system using 100x100x100 angstrom cell and a small central region of 10x10x10 angstroms is handled by GPAW. The central quantum box has a 2 angstrom transition region where the mixing weights change from 0.0 to 1.0 while moving inwards. In addition the GPAW calculation is performed with a 3 angstrom thick vacuum layer added around the actual quantum box zone. The purpose of this experiment is to show how the intra-molecule forces acting on the atoms change when the molecule enters and exits the quantum box. section 3.4. The calculations implement the force equation (2). The force components for a single hydrogen atom are shown in figure 4 which also shows how the forces gradually change from the values produced by ReaxFF to the ones computed by GPAW as the CH4 molecule enters the quantum box from the left. While it stays within the GPAW box the forces are constant, and then migrate back to ReaxFF values as it exits. Worth noticing is how the entry is completely smooth, but the exit has a sharp jump. This

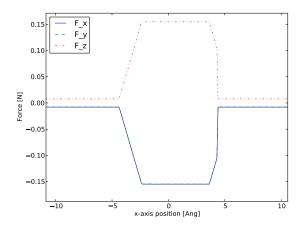


Figure 4: Force components acting on a methane hydrogen atom

is caused by Mixer making sure that all atoms of a single molecule are calculated with the same calculator. Now when the molecule is exiting, one of its atoms moves outside the GPAW calculation cell while the one being observed is still a significant distance from that boundary. At that point the entire molecule must be excluded from the GPAW computation. In other words the atom being inspected is on the trailing edge of the methane molecule. This discontinuity can be made less severe by using a larger transition region.

5 Conclusion

We have created a force and energy mixer for ASE. The Mixer framework was used to perform an ONIOM-like multiscale computation using GPAW and LAMMPS/ReaxFF and simple test scenarios were used to verify both energy and force mixing functionality. We have also created an ASE/LAMMPS interface designed to allow easy additions of new force fields. Current supported force fields include ReaxFF, CHARMM general force field, COMPASS and ClayFF. The MultiASE framework has proven to be flexible and robust enough in these simulations, and it is proposed here as a base for developing new and more advanced multiscale strategies.

6 Acknowledgments

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