QM/MM investigations of solvated water

Step 1: Preparation of the system involving generation of the restart and topology files for solvated water configuration and definition of the QM/MM partitioning

Step 2: Equilibration of solvent using dynamical simulations and optimizations

Step 3: Optimization of the entire system to obtain final stable configuration

Step 4: Excited state calculations on the final stable configuration using TD-DFT and EOM-CCSD methods

Comments:

- The only prerequisite for each step (except 1) is restart and topology files.
- Topology file generated in step 1 remains unchanged throughout the steps. ALl the coordinate changes are reflected in the restart file.
- Ideally, all the steps should be performed sequentially each providing updated restart file for the next simulation.
- Each step can be performed independently provided restart and topology files are copied from ./suppl subdirectory.
- Example output files for each step can be found in the output subdirectory

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Step 1: Preparation

The objective of this step is to generate restart and topology files for subsequent QM/MM simulations
In addition to input the following are required

- system coordinates in the form of the pdb file (h2o.pdb)
- fragment file (WTR.frg) that defines atom types for QM water
- parameter file (amber.par) to specify parameters for atom types in QM water

```
start h2o

prepare
source h2o.pdb
periodic
new_top new_seq
new_rst
center
orient
solvate box 2.0

modify segment 1 quantum
update lists
ignore
write h2o_ref.rst

write h2o_ref.pdb
end

task prepare
```

input pdb file

solvation in cubic 20 Å box

QM region definition

save restart file as h2o_ref.rst
topology file will be generated automatically as h2o.top

generate pdb file

Step 2: Equilibration

The objective of this step is to equilibrate solvent around QM water

In addition to input file the following are required

- topology file (h2o.top) generated in Step 1
- restart file (h2o_ref.rst) generated in Step 1

```
start h2o

memory total 1000 Mb
permanent_dir ./perm
```

Make copy of restart file

```
scratch_dir ./data

#make a copy of rst file
prepare
read h2o_ref.rst
write h2o_dyn.rst
end
task prepare
```

QM parameters

```
basis
 * library "6-31+G*"
end

dft
xc b3lyp
iterations 1000
end
```

MM parameters

```
md
 system h2o_dyn                                  1
 cutoff 1.0 qmmm 1.0
 noshake solute
 isotherm 0 298.15 anneal 0 3
 data 5000
 print step 100 stat 1000
 record rest 1000 prop 200
end
```

```
task qmmm dft energy                             2
```

QM/MM parameters

```
qmmm
region solvent
maxiter 3000
density espfit
end
```

```
task qmmm dft optimize                           3
task qmmm dft dynamics
```

Generate PDB file

```
prepare
read h2o_dyn.rst
write h2o_dyn.pdb
end
task prepare
```

Comments:

1. Classical parameters for dynamical simulation are specified in MD block. Dynamical simulation is ramped to constant room temperature over 3 ps. Output of dynamical simulation can be found in h2o_dyn.out
2. The first “task dft energy” is used to obtain wavefunction file to generate ESP charges for the QM region
3. The second “task dft optimize” optimizes solvent to remove any hot spots that may cause instabilities in dynamics
4. During dynamical simulation QM region is fixed and represented by ESP charges (“density espfit” in qmmm block)

Step 3: Optimization

The objective of this step is optimize the entire system. In addition to input file the following are required

- topology file (h2o.top) generated in Step 1
- restart file (h2o_dyn.rst) generated in Step 2

```
start h2o

memory total 1000 Mb
permanent_dir ./perm
scratch_dir ./data

prepare
read h2o_dyn.rst
write h2o_opt.rst
end
task prepare

basis
 * library "6-31+G*"
end
dft
xc b3lyp
iterations 1000
end


md
 system h2o_opt
 cutoff 1.0 qmmm 1.0
 noshake solute
end

qmmm
maxiter 20 3000
region qm  solvent
method bfgs sd
density espfit
xyz    h2o
ncycles 20
end


task qmmm dft optimize

#generate pdb file
prepare
read h2o_opt.rst
write h2o_opt.pdb
end
task prepare
```

Make copy of restart file

QM/MM optimization parameters

3

Comments:

1. Multi-region optimization is used cycling over qm and solvent regions (see qmmm block) 20 times (see ncycle). During each cycle QM region is optimized for 20 steps using BFGS optimization and solvent region is optimized for 3000 steps using steepest descent.
2. During solvent optimization QM region is represented by fixed ESP charges.
3. The progress of the optimization can be monitored by “grep @ output-file” for individual steps or “grep “@ total” output-file” only for cycles

Step 3: Excited state calculations

The objective of this step is to calculate excited of QM water in aqueous environment. In addition to input file the following are requiredrequired

- topology file (h2o.top) generated in Step 1
- restart file (h2o_opt.rst) generated in Step 3

```
start h2o

memory total 1000 Mb
permanent_dir ./perm

scratch_dir ./data

basis spherical
* library aug-cc-pvdz
end

dft
xc b3lyp
iterations 1000
end

md
 system h2o_opt
 cutoff 1.0 qmmm 1.0
 noshake solute
end
```

Include all the classical charges

```
qmmm
mm_charges expand all
end
```

TDDFT parameters

```
tddft
nroots 10
notriplet
end

task qmmm tddft energy
```

```
start h2o

memory total 1000 Mb
permanent_dir ./perm

scratch_dir ./data
```

HF reference wavefunction is used

```
basis spherical
* library aug-cc-pvdz
end

scf
thresh 1.0e-10
tol2e 1.0e-10
singlet
rhf
end
```

```
md
 system h2o_opt
 cutoff 1.0 qmmm 1.0
 noshake solute
end

qmmm
mm_charges expand all
end
```

Coupoled cluster parameters

```
tce
freeze atomic
ccsd
tilesize 20
diis 5
thresh 1.0d-5
2eorb
2emet 13
nroots 2
eomsol 1
end

task tce qmmm energy
```

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