QMQME-Pentacene

October 16, 2017

1 Study of the effect of the environment in the multipoles of Pentacene

We would like to study here the effects of the environment in the value of the elecrostatic dipole developed by a Pentacene molecule in cluster of various sizes.

```
In [1]: from BigDFT import Logfiles as L, Fragments as F
        import numpy as np
        import matplotlib.pyplot as plt
```

```
/usr/local/lib/python2.7/dist-packages/matplotlib/font_manager.py:273: UserWarning:
  warnings.warn('Matplotlib is building the font cache using fc-list. This may take
```

Let us first define the function that decompose the system into the fragment's quantities, and apply this function into the FullQM cluster:

```
In [2]: def get_pentacenes(filename):
            "Decompose the given system in pentacenes"
            RunLog=L.Logfile(filename)
            system=F.System(RunLog.electrostatic_multipoles,nat_reference=36,
                            units=RunLog.log['Multipole coefficients']['units'])
            print 'The system given by file "'\
                +filename+'" has ',len(system.fragments),' fragments'
            return system

        FullQM=get_pentacenes('log-FullQM.yaml')
```

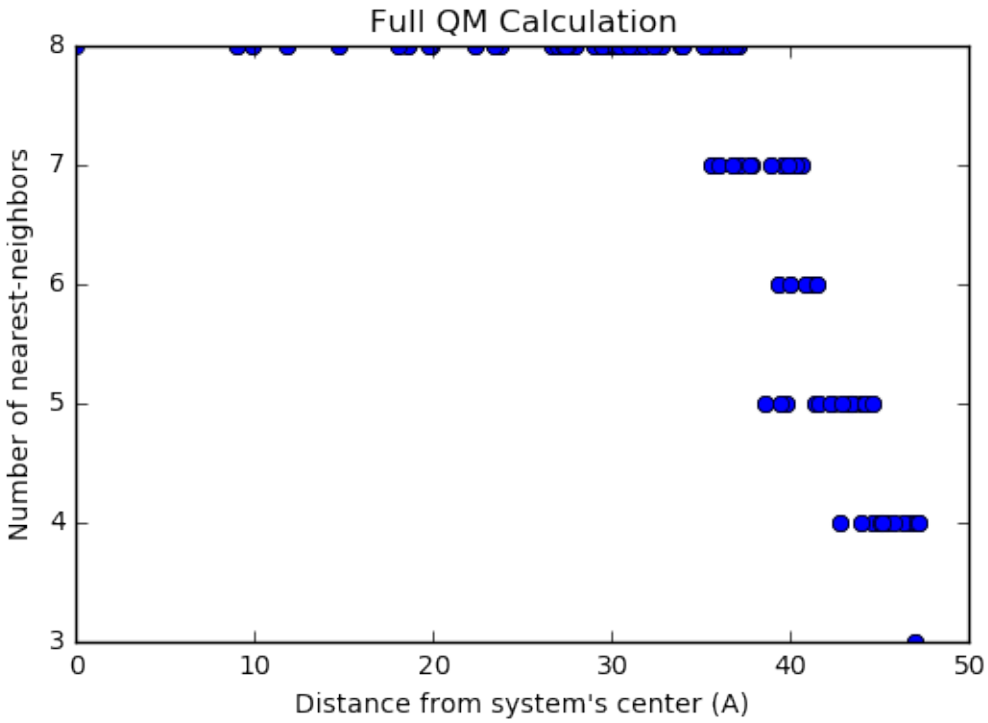
```
The system given by file "log-FullQM.yaml" has  191  fragments
```

Extract the list of nearest neighbors for the different fragments in the system

```
In [3]: #distance from system's centroid of all the fragments
        def distance_list(system):
            center=system.centroid()
            return [np.linalg.norm(r-center) for r in system.CMs]

        dist=distance_list(FullQM)
```

```
#use a naive quadratic scheme
DistancesPP=[np.array([F.distance(f,g) for g in FullQM.fragments])
             for f in FullQM.fragments]
#then calculate nbumber nearest-neighbors below a threshold
NNthr=15.0
NN=[]
for i,f in enumerate(FullQM.fragments):
    inn=0
    for g in DistancesPP[i]:
        if g< NNthr and g !=0.0: inn+=1
    NN.append(inn)
plt.plot(dist,NN,'o')
plt.xlabel("Distance from system's center (A)")
plt.ylabel("Number of nearest-neighbors")
plt.title('Full QM Calculation')
plt.show()
```

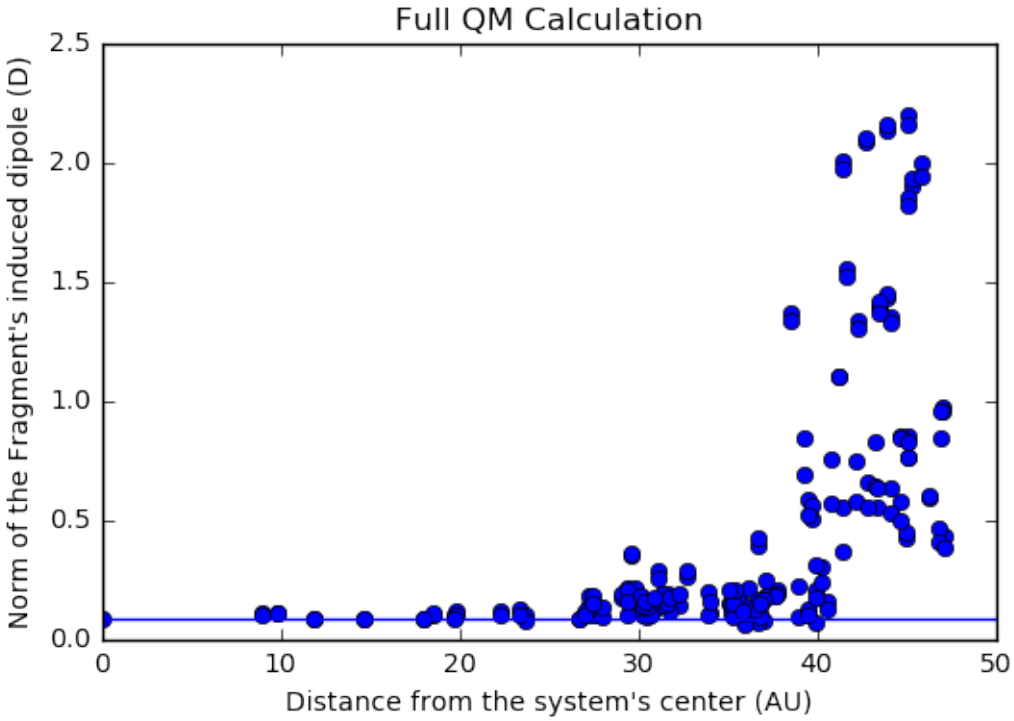


From the above plot we see that the there are surface Pentacenes that lie starting from about 30 A from the central fragment. Let us now correlate the surface effects with the norm of the dipole vector of the pentacene. In order to do that we compare the induced dipole of each of the system's fragments.

```
In [4]: d0=get_pentacenes('gasphase/log-1.yaml').fragments[0].d1()
        def dipole_list(system):
            return [np.linalg.norm(f.d1()-d0)/F.Debye_to_AU
```

```
                for f in system.fragments]
        dc=dipole_list(FullQM)[FullQM.central_fragment()]
        print 'Norm of the induced dipole on the central pentacene (D):',dc
        def analyse_system(system,label):
            plt.plot(distance_list(system),dipole_list(system),'o',label=label)
            plt.ylabel("Norm of the Fragment's induced dipole (D)")
            plt.xlabel("Distance from the system's center (AU)")
            plt.title('Full QM Calculation')
        analyse_system(FullQM,'FullQM')
        plt.axhline(dc,label='reference')
        plt.show()
```

```
The system given by file "gasphase/log-1.yaml" has  1  fragments
Norm of the induced dipole on the central pentacene (D): 0.0851493552668
```



It is clear from this figure that the "external" fragments, which are "close enough" to the surface of the cluster are strongly polarized by the environmental effects.

The internal fragments are weakly polarized. The induced dipole (ID) of the central Pentacene is only $8 \cdot 10^{-2}$ D. Still, such value can be found to all the internal fragments and it is therefore measurable. Let us now try to reproduce the same scenario in gas phase and with different embedding techniques.

```
In [5]: internal=20.0 # in AU (bohr)
        closest_PENs=np.where(np.array(distance_list(FullQM)) < internal)[0]
```

```
        closest_d1=np.array(dipole_list(FullQM))[closest_PENs]
        print 'Average ID for fragments closest than ',\
            internal,' bohr: \n',\
            np.mean(closest_d1),' +- ',np.std(closest_d1),' D'
```

```
Average ID for fragments closest than  20.0  bohr:
0.0962056942643  +-  0.0110042711852  D
```

```
In [6]: def fragment_dipoles(files,purgebeta=False):
            for f in files:
                print f
                #custom treatment for eliminate old non-yaml compliant line
                fl=f
                if purgebeta:
                    !cat $f | grep -v 'beta for' > tmp.yaml
                    fl='tmp.yaml'
                Cluster=get_pentacenes(fl)
                #print dipole_list(Cluster)
                d1=Cluster.fragments[Cluster.central_fragment()].d1()
                print 'Norm of induced dipole on central pentacene: ',\
                    np.linalg.norm(d1)
                analyse_system(Cluster,f)
```

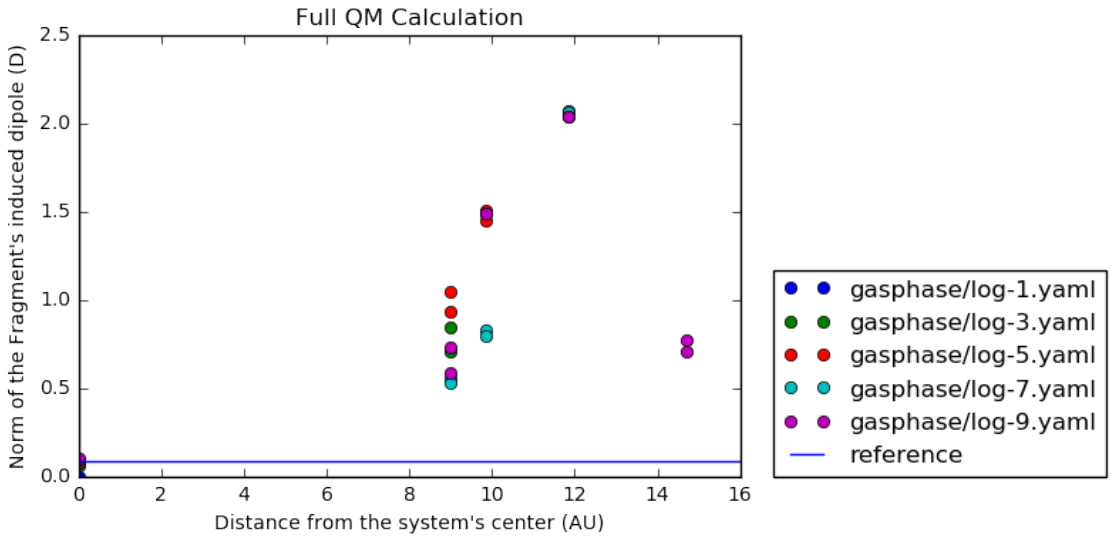
1.1 Gas phase fragments

We here analyse the dipoles of clusters of different sizes in the gas phase. We see that the central fragment develops a non-negligible dipole starting from a cluster of 9 molecules.

```
In [7]: files=!ls gasphase/log*.yaml
        fragment_dipoles(files)
        plt.axhline(dc,label='reference')
        plt.legend(loc=(1.05,0))
        plt.show()
```

```
gasphase/log-1.yaml
The system given by file "gasphase/log-1.yaml" has  1  fragments
Norm of induced dipole on central pentacene:  0.0769573922157
gasphase/log-3.yaml
The system given by file "gasphase/log-3.yaml" has  3  fragments
Norm of induced dipole on central pentacene:  0.0771618216795
gasphase/log-5.yaml
The system given by file "gasphase/log-5.yaml" has  5  fragments
Norm of induced dipole on central pentacene:  0.0840709958605
gasphase/log-7.yaml
The system given by file "gasphase/log-7.yaml" has  7  fragments
Norm of induced dipole on central pentacene:  0.097811546468
gasphase/log-9.yaml
The system given by file "gasphase/log-9.yaml" has  9  fragments
```

```
Norm of induced dipole on central pentacene:  0.100745796772
```



1.2 Averaged-environment fragments

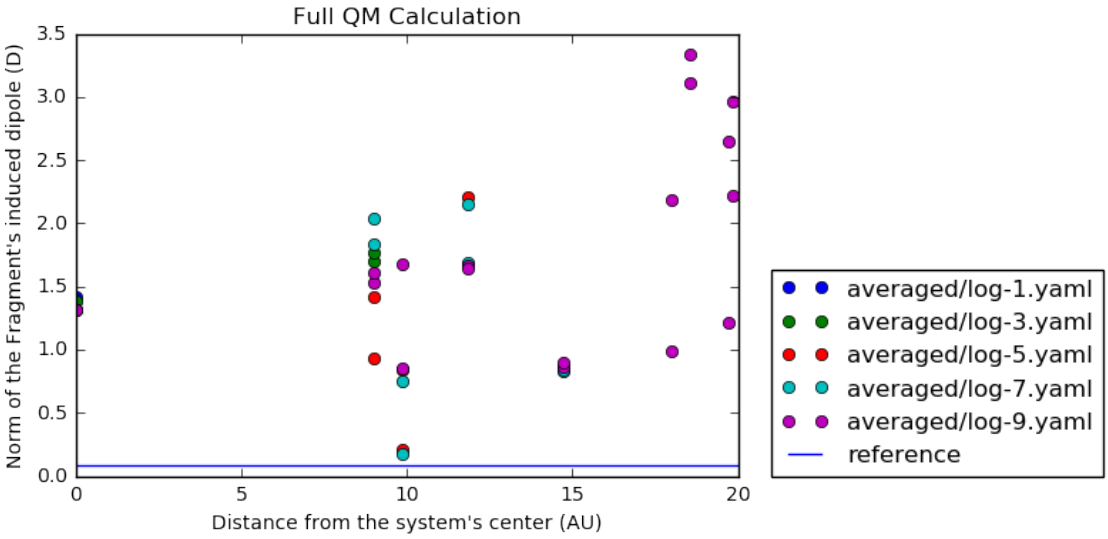
We then performed a calculation where a QM region of n fragments is embedded into an environment of $191 - n$ molecules. We assign to each of the environmental fragment the average values of he multipoles obtained from the molecules that are closer than 20 AU from the center, such as to avoid surface effects. Such treatment is detailed in the script QMMMBuild.py.

In this case, we see that the induced dipole is *too strong*: the *averaged* environment, even if taken from the very fragments belonging to the internal region, is *overpolarizing* the fragments. This phenomenon does not disappear, even for large clusters:

```
In [8]: #the list of the files is there
        files=!ls averaged/log-*
        fragment_dipoles(files,purgebeta=True)
        plt.axhline(dc,label='reference')
        plt.legend(loc=(1.05,0))
        plt.show()

averaged/log-1.yaml
The system given by file "tmp.yaml" has  1  fragments
Norm of induced dipole on central pentacene:  0.597523966672
averaged/log-3.yaml
The system given by file "tmp.yaml" has  3  fragments
Norm of induced dipole on central pentacene:  0.584482258604
averaged/log-5.yaml
The system given by file "tmp.yaml" has  7  fragments
Norm of induced dipole on central pentacene:  0.561455111032
```

```
averaged/log-7.yaml
The system given by file "tmp.yaml" has  9  fragments
Norm of induced dipole on central pentacene:  0.559292477972
averaged/log-9.yaml
The system given by file "tmp.yaml" has  17  fragments
Norm of induced dipole on central pentacene:  0.560940629534
```



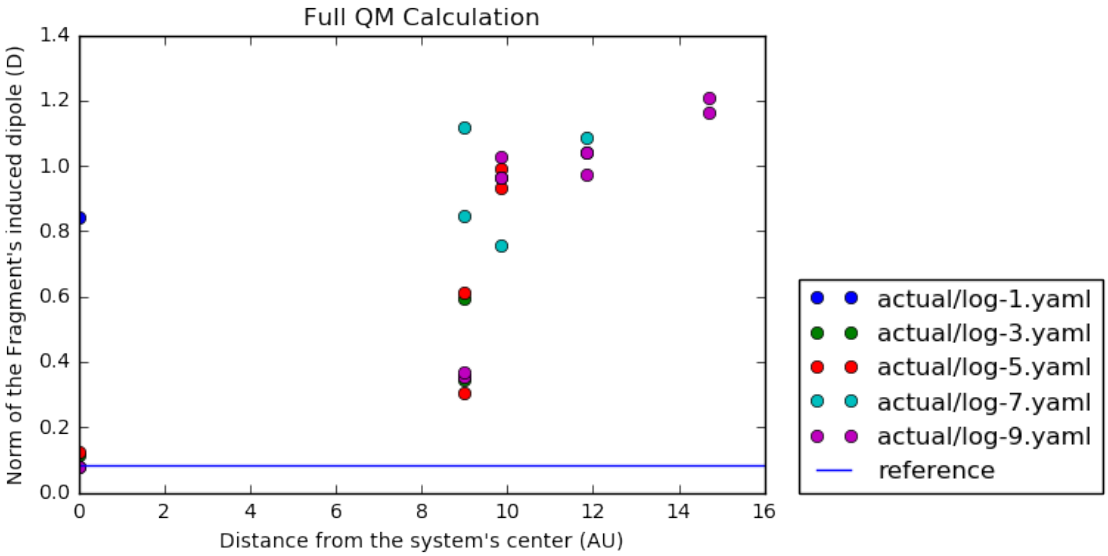
1.3 Fragment embedded in the actual QM/QMe environment

We have therefore considered the environment as the actual charges that each fragment generate on the QM region. In this case, things go at expected but *only* if we consider as QM region *at least* three pentacenes. Otherwise, for a single PEN the overpolarization phenomenon is still visible.

```
In [9]: files=!ls actual/log*.yaml
        fragment_dipoles(files)
        plt.axhline(dc,label='reference')
        plt.legend(loc=(1.05,0))#loc='upper left')
        plt.show()

actual/log-1.yaml
The system given by file "actual/log-1.yaml" has  1  fragments
Norm of induced dipole on central pentacene:  0.366799434796
actual/log-3.yaml
The system given by file "actual/log-3.yaml" has  3  fragments
Norm of induced dipole on central pentacene:  0.118622870262
actual/log-5.yaml
The system given by file "actual/log-5.yaml" has  5  fragments
Norm of induced dipole on central pentacene:  0.113074516037
```

```
actual/log-7.yaml
The system given by file "actual/log-7.yaml" has  7  fragments
Norm of induced dipole on central pentacene:  0.100643743578
actual/log-9.yaml
The system given by file "actual/log-9.yaml" has  9  fragments
Norm of induced dipole on central pentacene:  0.100451441055
```



Here we can immediately see that the actual environment is the one that is able to match the fullQM dipoles *but only when* at least 3 fragments are considered.