Geometric Descriptor Tutorial

Jolyon Aarons

October 11, 2017

Abstract

The descriptors we reported in [1] can be used to predict the catalytic activity of nanoparticles. In this tutorial, we will show how apply these techniques to model nanoparticles, specifically the cuboctahedral platinum Pt_{309} nanoparticle in these examples. The utilities required for these tasks are provided on the utilities section of the ONETEP website.

1 A Geometric Descriptor

Firstly, we will need a nanoparticle atomic coordinate file in .xyz format. The `Pt309.xyz` file is provided in the alphahull archive in the utilities section of the ONETEP website.

The goal of the first step will be to create an alpha-hull[5] from the coordinates of the atoms of the nanoparticle. An alpha-hull is the surface obtained if we were to take a ball of a given radius and roll it all around the atoms (assumed to be points) of a system, until no possible position of the ball where it is in contact with at least one point has been left. In practice we do not actually roll a ball, but use the algorithm of Edelsbrunner *et al* [5] using Delaunay triangulation [4] , for which we use the qhull library [2].

This will define our "surface" of the nanoparticle. Using the atoms on this surface, we then want to find all high-symmetry binding sites, such as hollow sites and bridge sites. We can then compute the generalized coordination number[3] of all of these sites together with the nanoparticle atoms which form the alpha-hull (which represent the atop binding sites). The alphahull utility will do all of this.

To run the example, we need to run the alphahull utility with `Pt309.xyz` as input. We also need a radius for the ball for the generation of the alpha-hull. This can either be left unspecified, in which case, the default of 2.1 Å will be used or given on the command-line as an argument.

```
alphahull -f Pt309.xyz -r 2.3 -v T
```

Here we have given the path to the `.xyz` coordinate file using the `-f` argument, the radius of the ball in Ångstroms, using the `-r` argument and stated that we want a *volumetric representation* of the alpha-hull using the `-v` argument, which is false by default.

This volumetric representation of the alpha-hull which is given as a Gaussian cube file is useful for checking that the ball radius is sensible, but takes much more time to generate, so it should be left disabled if it is not needed. This cube file represents how far a point in space is from the the closest point on

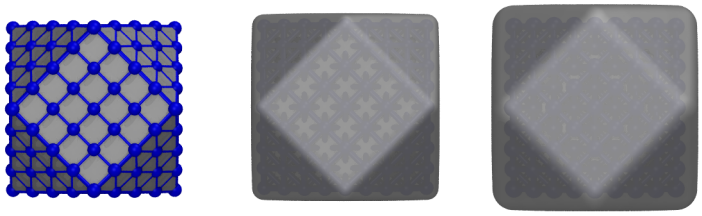

Figure 1: Increasingly high isovalue isosurfaces of the volumetric representation of the alpha-hull produced by the alphahull utility. Atomic coordinates are shown in blue and the isosurface is shown in silver. This isosurface represents the points in space which are a certain (the isovalue) away from the alpha-hull. Where the isovalue is zero (far left), the isosurface *is* the alpha-hull. (All atomistic figures were rendered with VMD Tachyon [7])

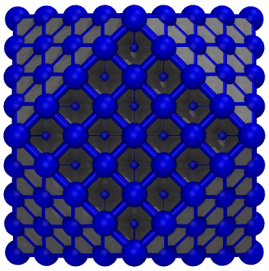

Figure 2: With too small a ball, the alpha-hull may have notches, or even holes.

the alpha-hull, therefore a zero isovalue isosurface of this data *is* the alpha-hull (see figure 1). If too small a ball is chosen in generating the alpha-hull, then it may pass between atoms of the system and form an undesirable alpha-hull with many holes (figure 2). If too large a ball is chosen, then surface roughness on the surface of the system will be averaged out. Some trial and error is necessary to find an adequate radius, but as a rule of thumb we start from 3/4 of the shortest atom-atom distance in the system and adjust it from there.

The volumetric output of alphahull is given as the seedname`_hull.cube`, where the seedname is the part of the original `seedname.xyz` file preceding the `.xyz` suffix.

The main output of alphahull is, however, the pdb file containing all possible binding sites on the system. This is given as the seedname`_allatoms.pdb`, where the seedname is again the part of the original `seedname.xyz` file preceding the `.xyz` suffix. Within this `.pdb` file are the coordinates of the platinum atoms on the surface of the alpha-hull, which correspond to atop binding sites projected onto the alpha-hull. Alternatively, these Pt sites may be simply viewed as the "surface" atoms of the nanoparticle. In the `.pdb` file are also three other coordinates labeled with "He", "Ho" and "Br". These correspond to (111) hollow sites, (100) hollow sites and bridge sites, respectively. In the `.pdb` file, there

are also values of coordination number and generalized coordination number for each site given in the occupancy and beta columns of the file (columns 9 and 10).

```
CRYST1      0.000      0.000      0.000  90.00  90.00  90.00 P 1
         1
ATOM       1  Pt    X     1           0.007   -7.827   -7.819  5.00  3.33
                  Pt
ATOM       2  Pt    X     1          -3.945   -3.956   -7.869  7.00  5.33
                  Pt
ATOM       3  Pt    X     1          -1.973   -5.907   -7.876  7.00  5.00
                  Pt
ATOM       4  Pt    X     1           0.005   -3.948   -7.916  8.00  6.50
                  Pt
.
.
.
ATOM     163  He    X     1          -1.313   -7.206   -7.198  6.33  4.05
                  He
ATOM     164  He    X     1           1.326   -7.204   -7.197  6.33  4.05
                  He
ATOM     165  He    X     1          -3.302   -5.273   -7.231  7.67  5.45
                  He
ATOM     166  He    X     1          -5.263   -3.314   -7.233  7.67  5.45
                  He
.
.
.
ATOM     291  Ho    X     1           0.006   -5.896   -7.872  6.75  4.23
                  Ho
ATOM     292  Ho    X     1           0.006   -7.878   -5.888  6.75  4.23
                  Ho
ATOM     293  Ho    X     1          -1.971   -3.947   -7.895  7.50  5.38
                  Ho
ATOM     294  Ho    X     1          -3.939   -1.982   -7.897  7.50  5.38
                  Ho
.
.
.
ATOM     387  Br    X     1          -4.946   -3.977   -6.909  8.00  5.67
                  Br
ATOM     388  Br    X     1          -3.966   -4.956   -6.909  8.00  5.67
                  Br
ATOM     389  Br    X     1          -1.973   -6.895   -6.887  7.00  4.44
                  Br
ATOM     390  Br    X     1          -2.980   -5.931   -6.912  8.00  5.56
                  Br
.
.
.
END
```

Listing 1: PDB of the Pt_{309} binding sites as calculated with the alphahull utility.

Using the `.pdb` file, we can plot these binding sites using a tool such as VMD [6]. For the Pt_{309} example, we can see all of the atop sites (plotted in figure 3). These as these sites are projected onto the alpha-hull, they are the positions of the surface platinum atoms (those that would be underneath the adsorbed oxgyen atom). To get actual binding sites, one would need to move along the average normal to each of the adjacent facets to the site by a distance of ~ 2 Å. This data can, therefore also be useful if we just want to know the surface

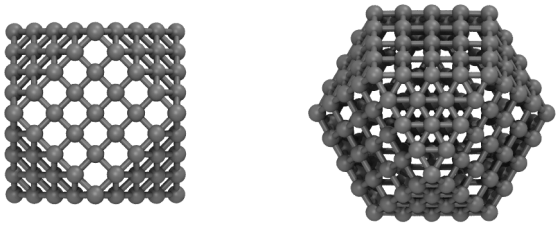

Figure 3: The surface platinum atoms of the Pt_{309} nanoparticle, which can alternatively be viewed as the atop binding sites projected onto the surface of the alpha-hull. A (100) facet is shown on the left and (111) on the right.

atoms of the system.

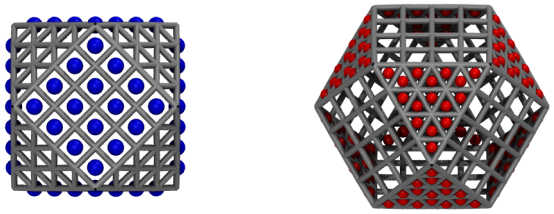

Figure 4: The hollow sites projected onto the alpha-hull of the Pt_{309} nanoparticle. The silver bonds show the positions of the surface platinum atoms for reference. On the left is shown one of the (100) facets with the hollow sites coloured blue, on the right is a (111) facet with the hollow sites coloured in red.

Similarly, we can see in figure 4 the positions of the hollow sites. These are separated into 3– and 4–fold hollow sites on the (111) and (100) facets respectively.

For bridge sites, there are several different types (111)–(100), (111)-(111) and (100)–(100), but these are not distinguished by the utility at the moment. We can however distinguish sites with greater detail by using the generalized coordination number using the beta channel of the `seedname_allatoms.pdb` file. We have done this for Pt_{309} in figure 6.

Once we have this data for binding site coodinates plus generalised coordination number for each site we can use a calibration curve which we have generated on a simple system spanning the range of binding energy. This simply means that we bind oxgyen (or the molecule of choice) onto a range of sites with generalized coordination number between 3 and 12 and do geometry relaxations and single-point energy calculations to determine the binding energy. We then plot binding energy against generalized coordination number and fit a

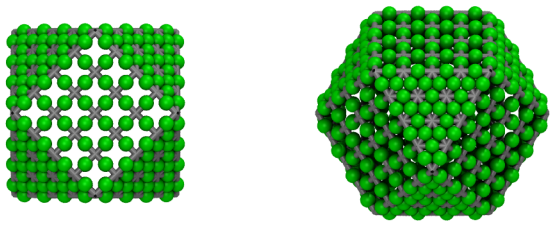

Figure 5: The sites projected onto the alpha-hull of the Pt_{309} nanoparticle. The silver bonds show the positions of the surface platinum atoms for reference. On the left is shown one of the (100) facets and on the right one of the (111) facets, both with the bridge sites highlighted in green.

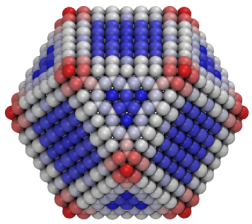

Figure 6: All binding sites projected onto the alpha-hull of the Pt_{309} nanoparticle, coloured by the generalized coordination number.

line through this data.

With this calibration curve, we can predict the binding strength of the molecule to sites on different, more geometrically complex systems (of the same composition) by giving the generalized coordination number as argument to predict the binding energy. This is described in more detail in [1] but for the purpose of this tutorial, our raw data for atomic oxygen binding on platinum is reproduced here in table 1.

Plotting this data as in figure 7, we get a calibration curve given by

$$E = 0.2569g - 2.4964, \tag{1}$$

where E is the predicted binding energy of an oxygen atom on a platinum nanoparticle site with generalized coordination number g.

In order to perform this process for our test nanoparticle, Pt_{309}, we have prepared a Matlab / Octave script, which is given in the alphahull archive on the ONETEP website. Once the generalized coordination numbers have been read into the workspace, a simple function such as the one given in listing 14 may be used to calculate our activity descriptor, which represents the proportion of the total binding sites which have a predicted binding strength within 0.2 eV of

Table 1: Tabulated DFT Site Data.

Site	Code	Location	gCN	n(e^-) (e/Å^3)	E_{bind} (eV)
Atop	A1	(111) on slab	*7.50*	0.0430	0.310
	A2	(111) mid facet Pt_{309}	*6.83*	0.0312	-0.590
	A3	(100) mid facet Pt_{309}	*6.67*	0.0325	-0.521
	A4	Edge site Pt_{309}	*5.33*	0.0200	-1.065
	A5	Vertex site Pt_{309}	*3.33*	0.0056	-1.704
	A6	Adatom on (100) Pt_{309}	*3.00*	0.0050	-1.725
	A7	Adatom on (111) Pt_{309}	*2.50*	0.0024	-1.638
	A8	(100) facet Pt_{309}	*6.58*	0.0320	-0.723
	A9	Edge site Pt_{309}	*5.00*	0.0180	-0.964
Bridge	B1	(100) mid facet Pt_{309}	*6.61*	0.0590	-1.405
	B2	(111) mid facet Pt_{309}	*5.56*	0.0600	-0.913
	B3	(111) on slab	*6.94*	0.0920	-0.411
	B4	(100)-(111) Edge site Pt_{309}	*4.94*	0.0510	-1.763
	B5	(111) facet Pt_{309}	*4.44*	0.0500	-1.124
	B6	Edge site Pt_{309}	*3.83*	0.0350	-1.620
Hollow	H1	(100) Pt_{309}	*6.46*	0.0960	-0.881
	H2	(111) HCP Pt_{309}	*6.68*	0.0830	-0.729
	H3	(111) FCC Pt_{309}	*5.41*	0.0740	-1.213
	H4	(111) FCC on slab	*6.95*	0.1100	-0.751
	H5	(111) HCP on slab	*7.50*	0.1130	-0.472
	H6	(111) HCP edge Pt_{309}	*5.45*	0.0780	-1.329
	H7	(111) HCP vertex Pt_{309}	*4.05*	0.0630	-1.471

the predicted optimum binding energy. This descriptor can be applied easily to large numbers of systems with many atoms very quickly and is easy to modify for other FCC metals than platinum / other molecules.

```
function SABE=master_curve(gencoord_atop, gencoord_bridge,
    gencoord_hollow)
% Apply calibration curve
gencoord=[gencoord_atop, gencoord_bridge, gencoord_hollow]';

gencoord(isnan(gencoord)) = [] ;

all_energies = 0.2569*gencoord - 2.4964 ;
good_energies = all_energies ;
good_energies(good_energies>-0.32) = [] ;
good_energies(good_energies<-0.72) = [] ;
SABE = size(good_energies)/size(all_energies)

end
```

Listing 2: A Matlab / Octave script to apply the calibration curve to predict binding strengths and to find the proportion of binding sites within 0.2 eV of the catalytic optimum binding strength (0.52 eV in this case).

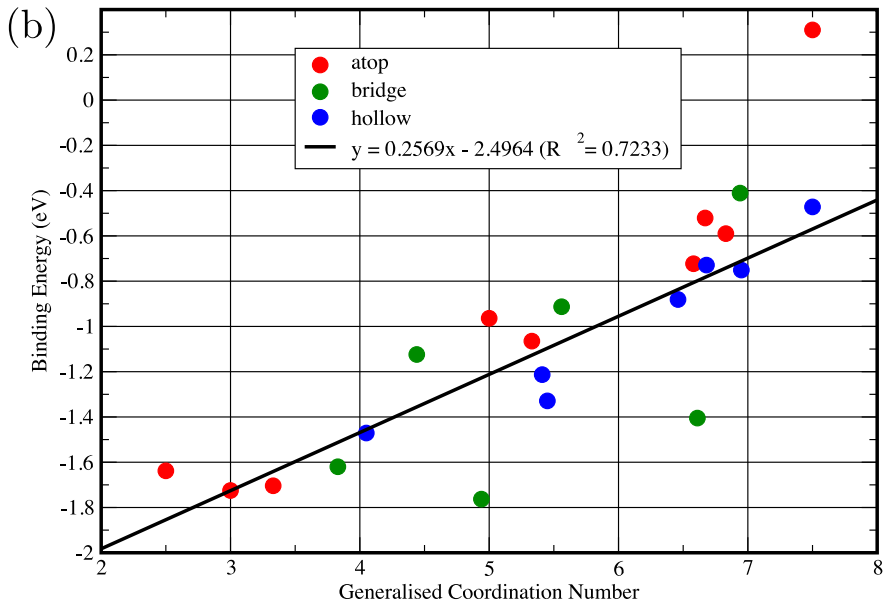

Figure 7: Calibration curve for oxygen on platinum, DFT binding energy calculations versus generalized coordination number.

References

[1] J. Aarons, L. Jones, A. Varambhia, K. E. MacArthur, D. Ozkaya, M. Sarwar, C.-K. Skylaris, and P. D. Nellist. Predicting the oxygen-binding properties of platinum nanoparticle ensembles by combining high-precision electron microscopy and density functional theory. *Nano Letters*, 17(7):4003–4012, 2017. PMID: 28644034.

[2] C. B. Barber, D. P. Dobkin, and H. Huhdanpaa. The quickhull algorithm for convex hulls. *ACM Transactions on Mathematical Software (TOMS)*, 22(4):469–483, 1996.

[3] F. Calle-Vallejo, J. I. Martnez, J. M. Garca-Lastra, P. Sautet, and D. Loffreda. Fast prediction of adsorption properties for platinum nanocatalysts with generalized coordination numbers. *Angewandte Chemie International Edition*, 53(32):8316–8319, 2014.

[4] B. Delaunay. Sur la sphère vide. a la mémoire de georges voronoï. *Bulletin de l'Académie des Sciences de l'URSS. Classe des sciences mathématiques et na*, 1934(6):793–800, 1934.

[5] H. Edelsbrunner, D. Kirkpatrick, and R. Seidel. On the shape of a set of points in the plane. *IEEE Transactions on Information Theory*, 29(4):551–559, July 1983.

[6] W. Humphrey, A. Dalke, and K. Schulten. VMD – Visual Molecular Dynamics. *Journal of Molecular Graphics*, 14:33–38, 1996.

[7] J. Stone. *An Efficient Library for Parallel Ray Tracing and Animation*. Master's thesis, Computer Science Department, University of Missouri-Rolla, April 1998.