Meeting with SLAC people

June 17, 2011

Background information

Small Au nanoclusters

- Planar structures ($N < 12$)
- Cage-like structures
- Tetrahedron ($N = 20$)
- Various low-symmetry structures...

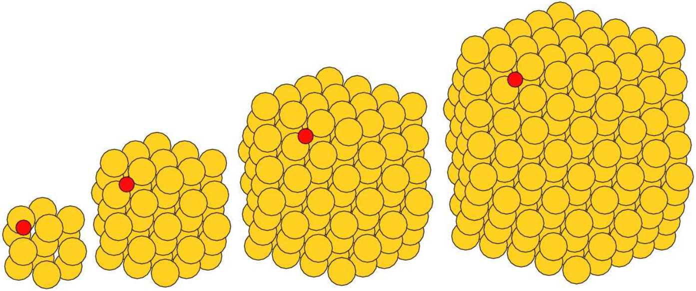
Large Au clusters

- Icosahedra
- Truncated octahedra

Also depends on temperature, etc. We don't want to mess with all the complicated structures. Rather we consider some simpler, more regular systems.

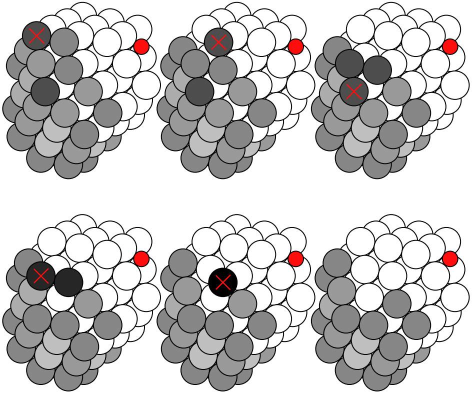
Geometric shells

- Consider a central atom, and then add complete shells of atoms around that atom
- If atoms are added on fcc lattice sites, we get the cuboctahedra with $N = 13, 55, 147, 309, 561, 923, 1415, \ldots$



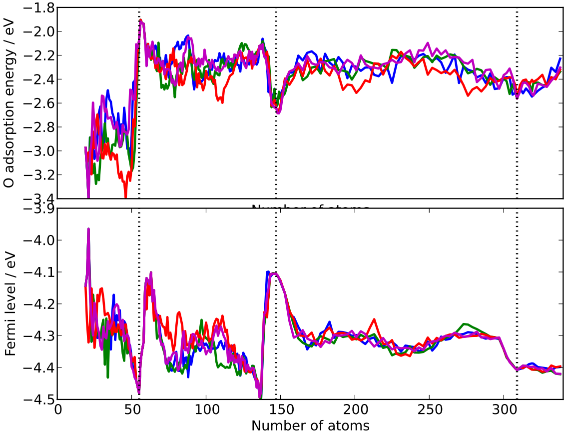
Above: The first gold cuboctahedra and some oxygen

Peeling off atoms



- Start with one cuboctahedron
- Find atoms with lowest coordination
- Remove one of those at random
- Repeat as necessary until smaller cuboctahedron remains

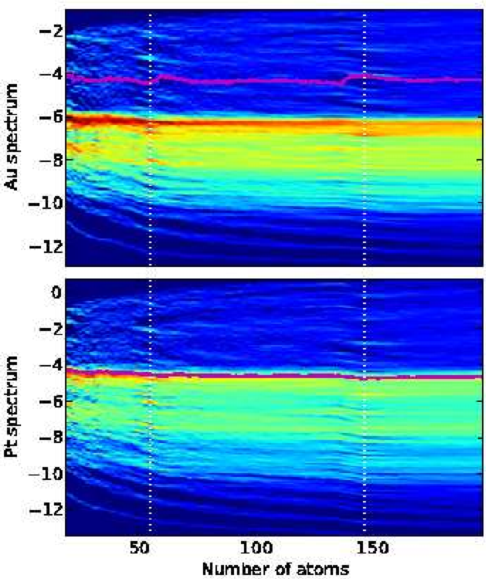
- We use this method to generate large amounts of clusters of different size
- Tends to remove corner atoms and whole facets



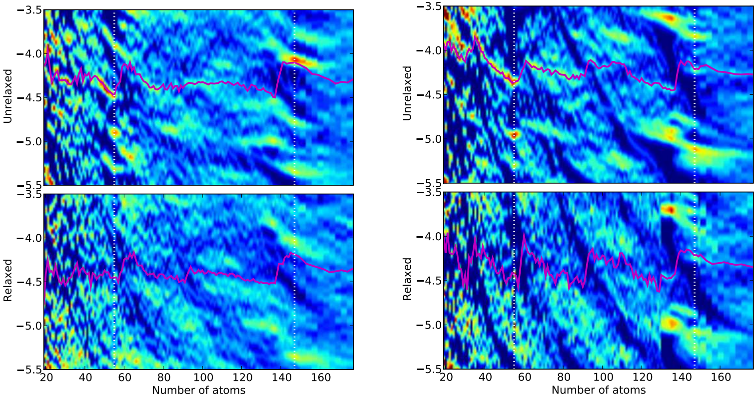
Adsorption energy as a function of cluster size. Different colours are different random seeds, i.e. ways in which to remove atoms. Below is variation of Fermi level

Electronic structure of Au and Pt clusters

- Figure: DOS as a function of cluster size and energy. Red = large DOS.
- Au: Fermi level (purple) well above d-band
- Pt: Fermi level at top of d-band
- For Au, gaps in spectrum around Fermi level

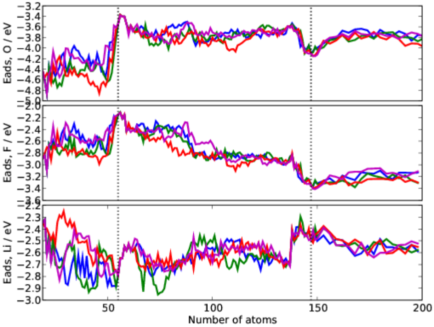


Au cluster DOS and relaxation effects



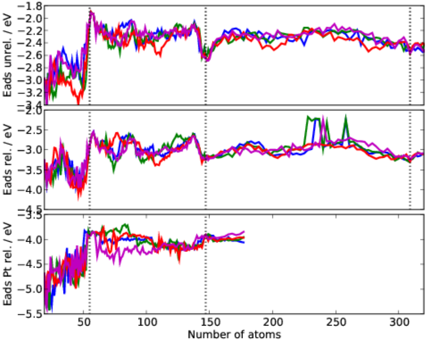
- Spectrum before and after relaxation for cuboctahedra (left), icosahedra (right). Structure is enhanced by relaxation.
- Magic numbers 34, 58, 92, 138

Adsorption energies



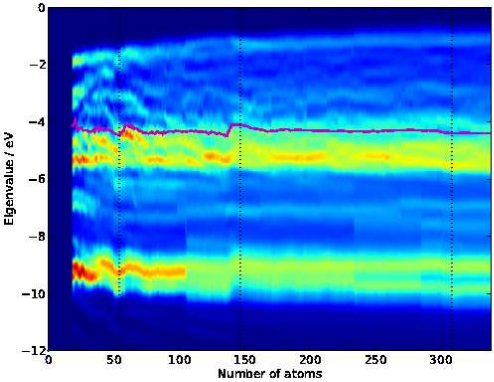
- Adsorption energies as a function of cluster size for O, F, Li with different randomly generated clusters (colours)
- Jumps at 58 and 138 correspond to electronic magic numbers
- Opposite behaviour for Li vs O/F hints at alkali/halogen-like properties of clusters around magic numbers
- (clusters are unrelaxed. Forgot to subtract atomic reference energies so all graphs should be shifted...)

Relaxed clusters and comparison to Pt



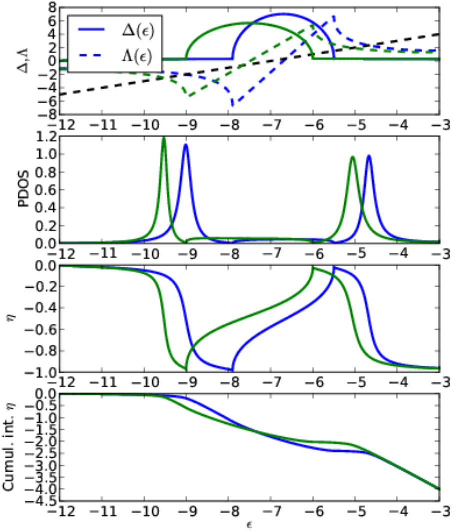
- O on relaxed Au / Pt clusters
- Smaller clusters bind more strongly
- Most variations for Pt coincide with variations of local geometry
- For Au, local geometry and magic both significant

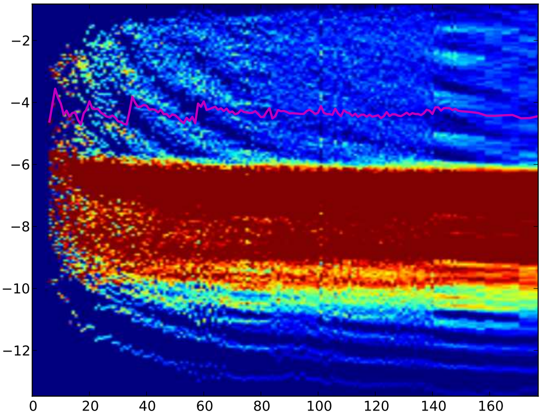
Projected density of states on O



- Projected density of states on O atom
- Split into bonding/antibonding states, all of which are filled
- Since the antobonding states do not become unoccupied, so that won't explain the stronger bonding on smaller clusters.

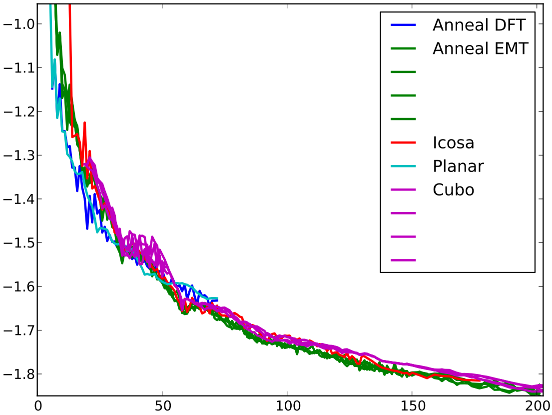
- Assume V_{ak} behaves like semielliptic d-band and s-band
- (Δ is V_{ak} recast as a continuous function)
- Move d-band, see what happens (blue / green in Figure)
- Conclusion: if $\epsilon_F > -4.5$, d-band does not affect adsorption energy



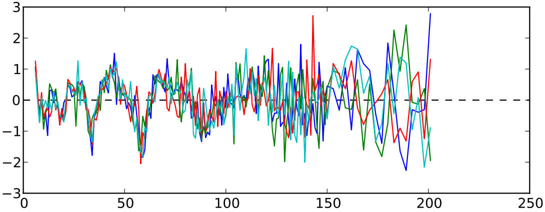


DOS of clusters obtained by simulated annealing with EMT

EMT relaxations

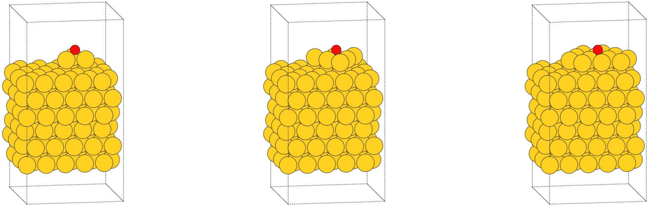


Energy per atom. EMT-relaxed clusters generally have lowest energies, except for very small clusters with linear structures etc

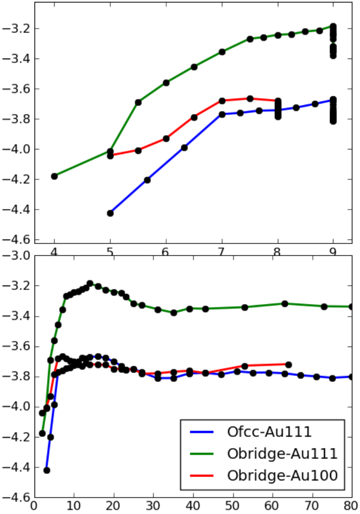


Energy minus fitted trendline ($a * N^{1/3} + \ldots$ etc.)

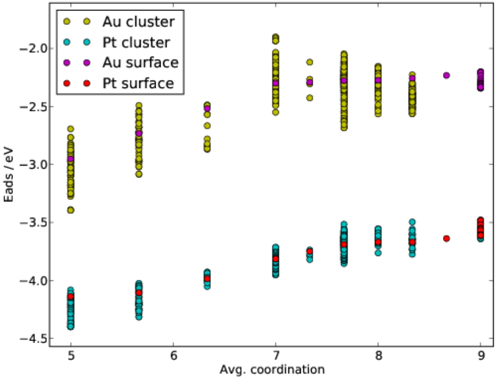
Analysis in terms of facet sizes and local coordination

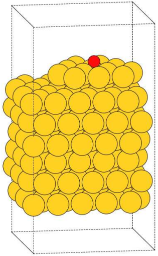


- Calculate adsorption energy on plateaus of various size
- This might distinguish global electronic structure effects (magic numbers and such) from purely geometric effects



Binding energy as a function of avg. neighbour coordination (top) and plateau size in atoms (bottom) on different Au surfaces





- Adsorption energy as a function of the average coordination number of the adsorbates' neighbouring metal atoms
- Au surface binding decreases with coordination up to 7 (coinciding with a 55 cluster facet), but eventually reverses.
- Pt binding more regular.