

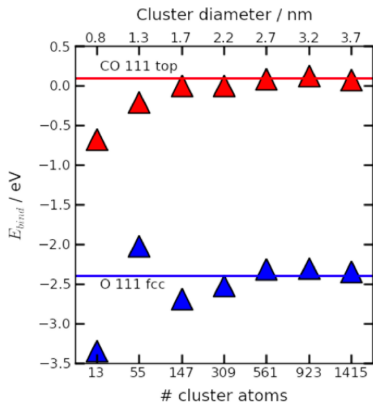
Gold nanoclusters and quantum-size effects

Ask Hjorth Larsen

CAMD review meeting

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Oxygen adsorption on gold clusters



- ▶ What's going on with the 55-atom cluster?
- ▶ DFT is complicated. Let's instead construct a simple model, and everything will be as clear as the queue to the Opteron nodes during the summer vacation. (Spoiler alert: no it won't)

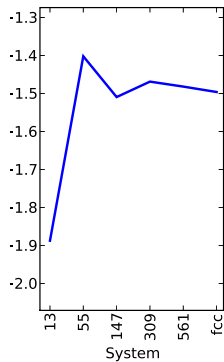
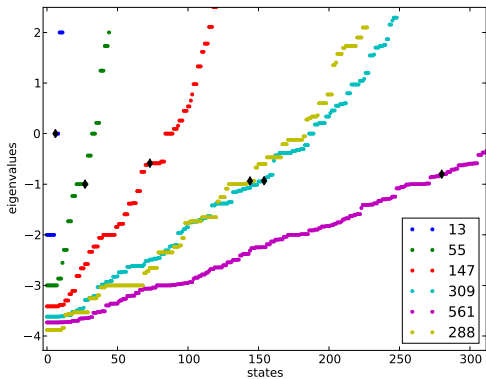
Tight-binding model

Assume one electron per Au and one for O and construct a Hamiltonian with only nearest-neighbour interactions.

TB Hamiltonian

- ▶ Au on-site elements (can defined to be 0)
- ▶ Adsorbate level ϵ_a
- ▶ Au-Au neighbour hopping element η
- ▶ Au-O neighbour hopping element t

This matrix can then be diagonalized, and energies can be added up to the Fermi level to obtain a total energy.



Left: Eigenstates of clusters. Right: Adsorption energies.

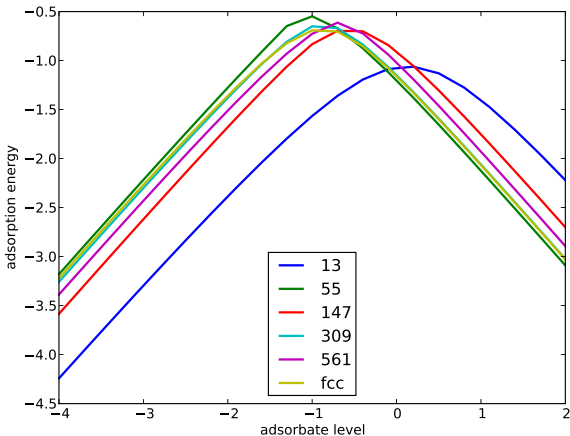


Figure: Adsorption energies as a function of adsorbate level ϵ_a . Limiting behaviour $E_{\text{ads}} \approx |\epsilon_a - \epsilon_F|$ for $|\epsilon_a| \gg |t|$ (assuming neutrality of subsystems). Importance of Fermi level is slightly suspicious as this doesn't seem to match DFT.

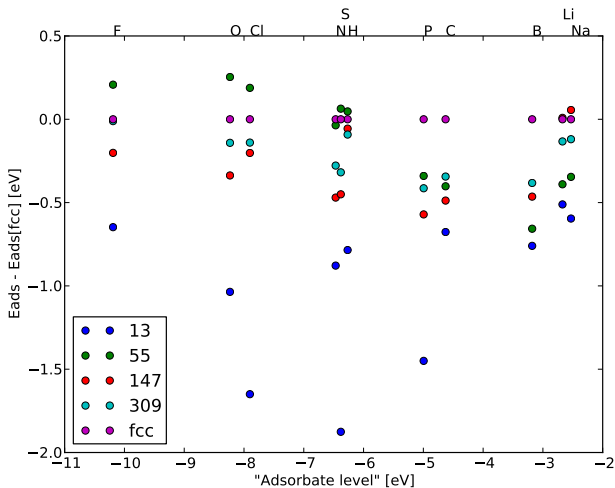


Figure: DFT adsorption energies (bulk defined to 0) for different elements as a function of "adsorbate level" (HOAO level of isolated atom). LCAO mode, unrelaxed geometries

Newns-Anderson model

- ▶ A Hamiltonian which describes the interaction between a one-electron adsorbate and a solid:

$$H = H_0 + V$$
$$H_0 = \sum_k \epsilon_k c_k^\dagger c_k + \epsilon_a c_a^\dagger c_a$$
$$V = \sum_k v_{ak} c_a^\dagger c_k + h.c.$$

- ▶ Parameters are the continuous spectrum ϵ_k of the solid, the adsorbate level ϵ_a and the coupling v_{ak} .
- ▶ The model has only one electron on the adsorbate, so we consider H adsorption in the following
- ▶ Due to double-count energy corrections (everything except the Kohn-Sham eigenvalues) it is not obvious how to adapt a DFT-based Hamiltonian for a Newns-Anderson model

Adsorption energy in Newns-Anderson model

- ▶ Adsorption energy can (eventually) be expressed as an integral of a “phase shift” over all occupied states

$$E_{\text{ads}} = \int_{-\infty}^{\epsilon_F} \eta(\epsilon) d\epsilon$$

- ▶ Reveals how much the individual states contribute to adsorption energy shift

Newns-Anderson Hamiltonian from DFT

“Cutting corners”

- ▶ Perform a DFT calculation to get Hamiltonian $H_{\mu\nu}$ in LCAO basis
- ▶ Grab the blocks:

$$H = \begin{bmatrix} H_K & T_{KA} \\ T_{AK} & H_A \end{bmatrix}$$

- ▶ Diagonalize H_K and the atomic states H_A independently to get ϵ_k and ϵ_a plus transformation matrices C_K and C_A .
- ▶ Now the interactions are given by

$$V_{KA} = C_K^\dagger T_{KA} C_A$$

- ▶ Drawback: Adsorbate states are not orthogonal on cluster states, so this is somewhat wrong and also can't readily be put into a Newns-Anderson model

Newns-Anderson Hamiltonian from DFT

“Handmade” Hamiltonian

- ▶ Perform two DFT calculations: adsorbate and cluster.
- ▶ Construct the matrix:

$$H = \begin{bmatrix} H_K & T_{KA} \\ T_{AK} & H_A \end{bmatrix}$$

where H_K and H_A come from the cluster and adsorbate calculation, and T_{KA} are generated by using the sum of the local potentials from adsorbate and cluster $\langle \Phi_a | v_A + v_K | \Phi_k \rangle$.

- ▶ Now the interactions can be found as before:

$$V_{KA} = C_K^\dagger T_{KA} C_A$$

- ▶ This (almost) gets all the PAW corrections correct, but the eigenstates are still not orthogonal. We must explicitly transform the cluster states to orthogonalize them on the adsorbate.

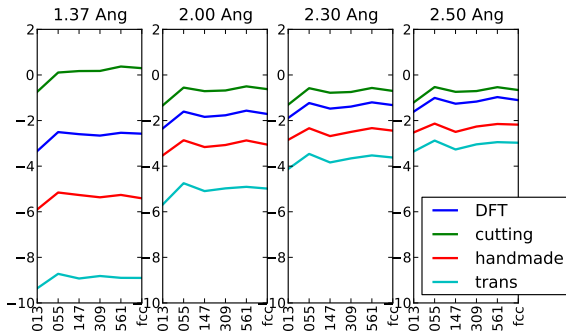


Figure: Adsorption energies with different ways of constructing NA Hamiltonian from DFT eigenvalues for different clusters and different adsorbate-cluster distances

Conclusion

- ▶ So that's how one might use a Newns-Anderson model based on DFT PAW LCAO calculations!
- ▶ LCAO mode is fast, woohoo
- ▶ But we still don't really understand the quantum-size effects.