Efficient electronic structure methods applied to metal nanoparticles

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Overview

- This is a theoretical project based on computer calculations
- We develop an efficient method to calculate the properties of matter at the atomic scale
- Then we apply the method to understand the chemistry and other properties of metal nanoparticles or clusters

What are clusters?

- Particles with a few to a few thousand atoms
- “Typical” size 1–10 nanometres
- It turns out that small clusters may behave very differently from bulk materials
- This makes clusters interesting, for example in catalysis

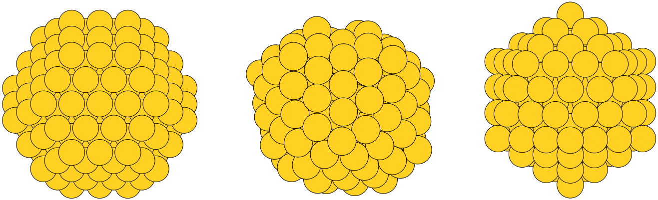
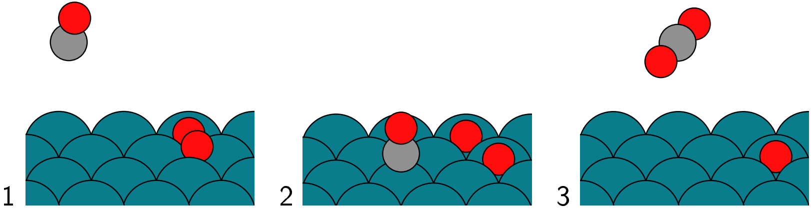


Figure: Examples of possible cluster structures

Catalysis

- A catalyst increases the rate of a reaction without being consumed in it
- Example: $2\ \mathrm{CO} + \mathrm{O}_2 \longrightarrow 2\ \mathrm{CO} + 2\mathrm{O} \longrightarrow 2\ \mathrm{CO}_2$



- In this example, the catalyst helps split O_2
- Design of better catalysts requires an understanding of matter at small scales

Quantum mechanics

- Atomic-scale systems are described by quantum mechanics. In principle we could calculate all of chemistry by solving the Schrödinger equation
- These calculations are expensive and may take days. Therefore we use supercomputers

An electronic structure calculation

1. Define the locations of atoms
2. The computer solves the electronic problem, obtaining electron density, wavefunctions and electronic energies
3. The computer spits out energy, forces on atoms, ...

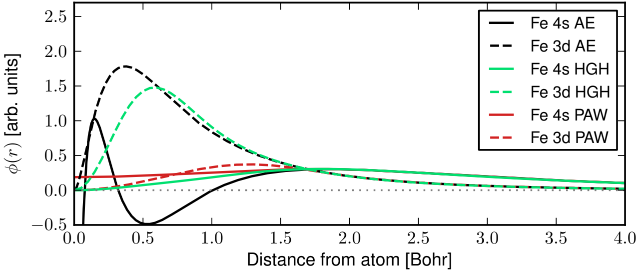
Density functional theory

- An approach to first-principles electronic structure calculations based on the electron density as fundamental variable
- Unique compromise between accuracy and performance
- Most of this work is based on DFT calculations

Iterative procedure

- Calculate electron density from wavefunctions
- Calculate potential from density
- Solve for wavefunctions given the potential

The quest for smooth wavefunctions



- Wavefunctions oscillate and are expensive to represent
- Remove core electrons, replace nuclei with pseudopotentials
- PAW: Extension to pseudopotentials. Avoids norm-conservation, and retains “all-electron” information

Localized basis sets in PAW

As implemented in GPAW

Method

- Choose a basis of localized atomic orbitals $|\Phi_\mu\rangle$
- Expand wavefunctions as

$$|\tilde{\psi}_n\rangle = \sum_\mu |\Phi_\mu\rangle c_{\mu n}$$

- Results in generalized eigenvalue problem

$$\sum_\nu H_{\mu\nu} c_{\nu n} = \sum_\nu S_{\mu\nu} c_{\nu n} \epsilon_n$$

Pros

- Can use direct matrix diagonalization
- Localization improves scaling of many operations

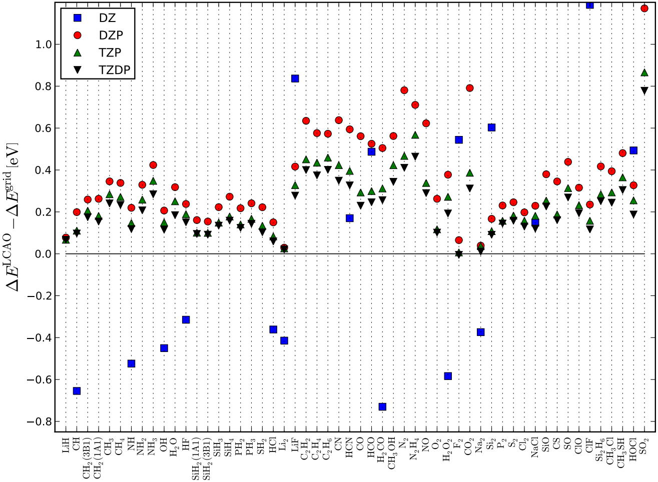
Cons

- Less accurate than real-space or plane-wave representation, particularly for binding energies

A quick review

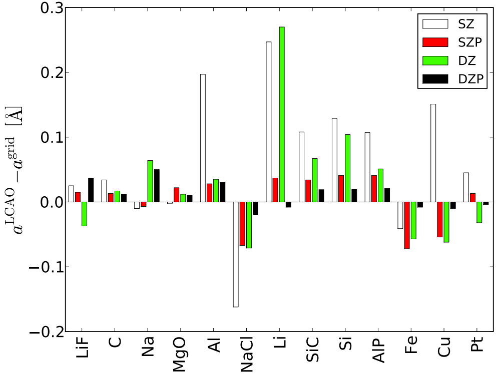
- Localized basis sets: A cheap representation of wavefunctions
- Projector augmented wave method: Complicated but efficient approach to density functional theory
- Density functional theory: An efficient approach to computational quantum mechanics
- Quantum mechanics: Predicts the properties of matter at small scales.

Atomization energies



A. H. Larsen, M. Vanin, J. J. Mortensen, K. S. Thygesen, and K. W. Jacobsen. Phys.Rev.B, vol. **80**, p. 195112, 2009.

Lattice constants



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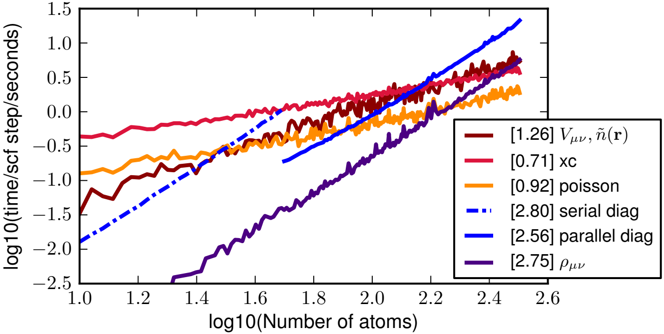
Operation	Parallelization	Complexity
Multigrid Poisson	$\mathbf{r}$	$\mathcal{O}(N)$
Density $\tilde{n}(\mathbf{r})$	$\mathbf{r}$, σ	$\mathcal{O}(N)$
XC $\tilde{v}_{\mathrm{xc}}(\mathbf{r})$	$\mathbf{r}$, σ	$\mathcal{O}(N)$
Potential $V_{\mu\nu}$	ν, $\mathbf{r}$, σ, k	$\mathcal{O}(N)$
Diagonalize $H_{\mu\nu}$	μ, ν, σ, k	$\mathcal{O}(N^3)$
Density matrix $\rho_{\mu\nu}$	μ, ν, σ, k	$\mathcal{O}(N^3)$



Part II

In which we perform a large number of calculations on clusters

Motivation

- Metal clusters are good catalysts
- Clusters are large and computationally expensive
- We study the reactivity of clusters by calculating adsorption energies of simple adsorbates using a combination of overwhelming computational power and cheap methods

Large clusters: Atomic shells and packing

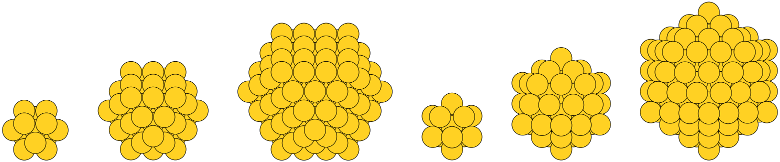


Figure: The first few cuboctahedra and icosahedra (N=13, 55, 147, ...)

- Cuboctahedra are consistent with FCC packing
- Icosahedra have more (111) surface, but are strained

A likely series of structural motifs as size increases is icosahedra→ decahedra→ truncated octahedra/cuboctahedra

Towards the bulk limit

Figure: BlueGene/P supercomputer. Our largest calculations use 32768 or 65536 CPUs (Source: Flickr, by "Argonne National Laboratory").

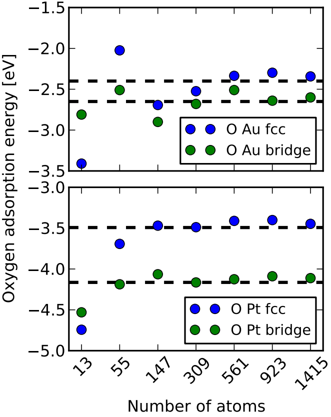


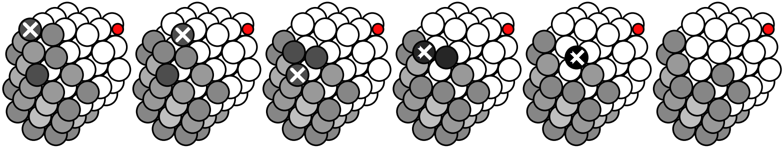
Figure: Adsorption energy of oxygen on Au and Pt cuboctahedra

Studying quantum-size effects

- We want to study electronic size effects on chemisorption using simple model systems
- Plan: Build a large ensemble of clusters and run fast LCAO calculations

Construction of clusters

- Remove atoms one at a time from one cuboctahedron until a smaller cuboctahedron remains



Size effects in transition metals

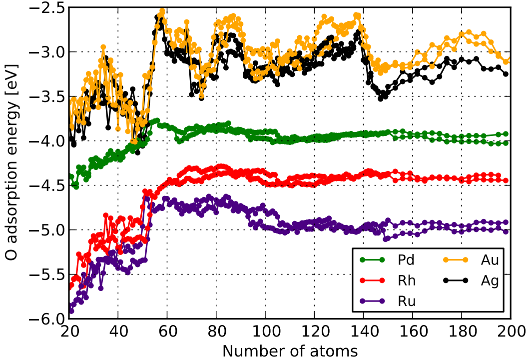


Figure: Adsorption energies of oxygen on different transition metals

s^1d^7	s^1d^8	s^1d^9	s^1d^{10}	s^2d^{10}
Fe	Co	Ni	Cu	Zn
Ru	**Rh**	**Pd**	**Ag**	Cd
Os	Ir	Pt	**Au**	Hg

- Smooth variations can be attributed to "geometric effects"
- Metals with full d-shell show strong oscillations

Shell structure and magic numbers

- Consider N non-interacting electrons in a spherical well
- Solve analytically for electronic energies and degeneracies

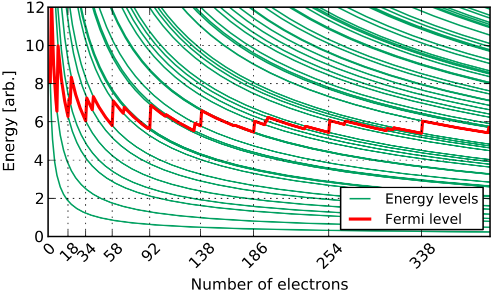


Figure: Electronic states of “jellium” clusters showing shell structure. High stability at shell closings give rise to so-called magic numbers

- Jellium shell structure well known from alkali metal clusters

Electronic structure of metal clusters

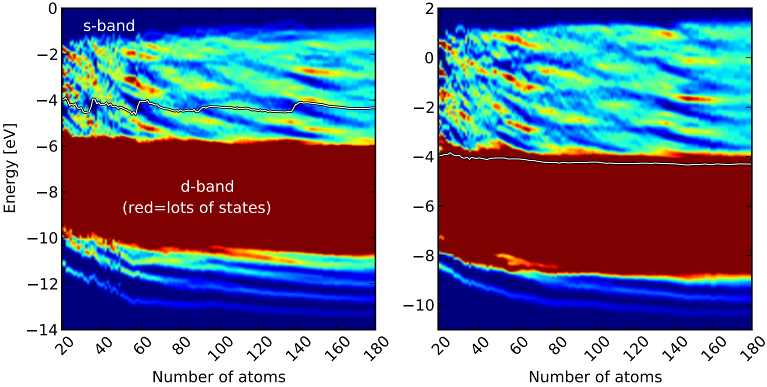
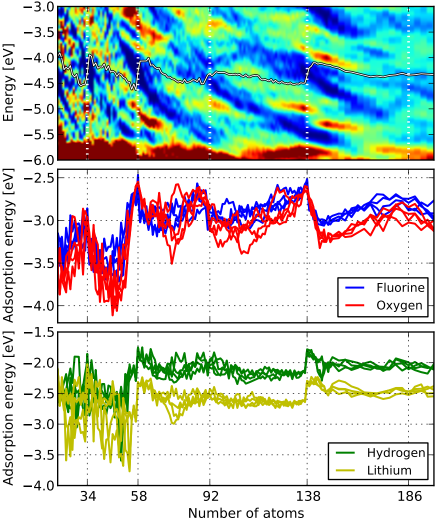


Figure: Energy distribution of electronic states for gold (left) and palladium (right) as a function of cluster size, showing electronic shell structure. The line indicates the Fermi level

Chemisorption on gold clusters

- Reactivity follows magic numbers
- Electronegative adsorbates (O, F) bind strongly to clusters just above magic numbers
- Electropositive ones (H, Li) do the opposite

(Actually, H would be expected to take, rather than give, an electron. But the explanation is too hairy for now)



Global structure optimizations

- We can find the low-energy structures of gold clusters using molecular dynamics with simulated annealing
- Simulate movements of each atom at high temperature
- Slowly lower temperature until cluster freezes
- Expensive—requires thousands of calculations

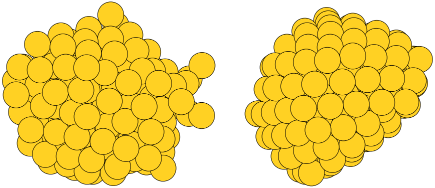
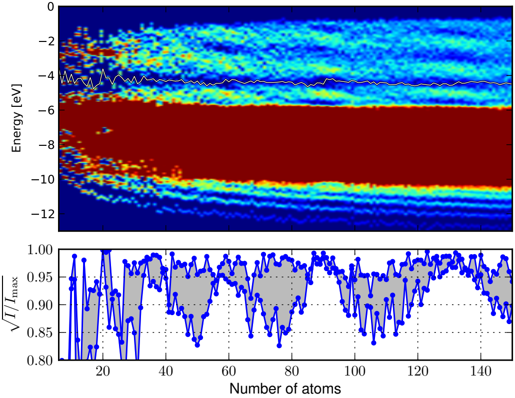


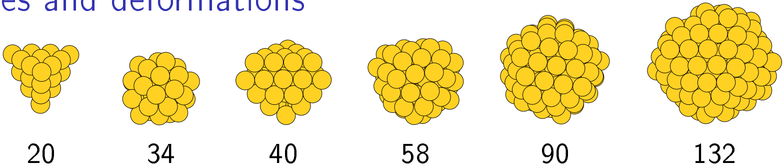
Figure: Cluster at 750 K and 0 K

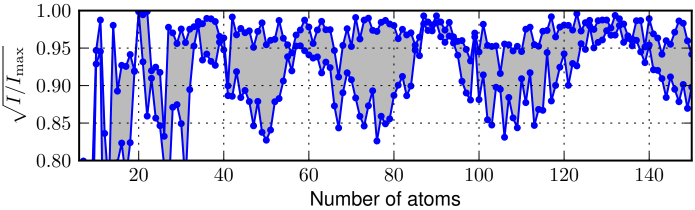
Electronic versus geometric structure

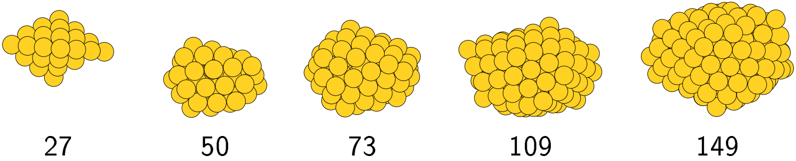
- Right: Electronic structure of gold clusters from simulated annealing with DFT
- Below: Deformations calculated from moments of inertia
- Clusters deform to create electronic gaps well beyond 100 atoms



Shapes and deformations







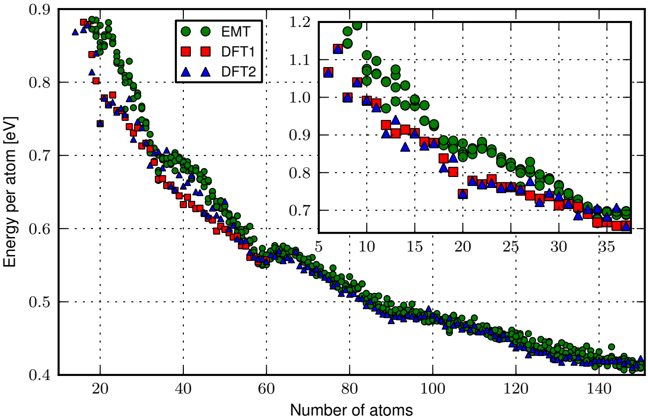


Figure: Energy per atom of clusters, with structures determined using DFT vs EMT (ASAP).

Conclusions

- Localized basis sets are very well suited for studying broad trends and large ensembles of systems
- The reactivity of noble-metal clusters with hundreds atoms in size is entirely dominated by global electronic shell effects
- The reactivity of non-noble transition metal clusters converges much faster with size, and follows variations of local geometry
- The structure of gold clusters well beyond 100 atoms is intricately dependent on electronic effects