The Importance of being the right shape

Interplay of Geometric and Electronic Structures in Atomic Clusters

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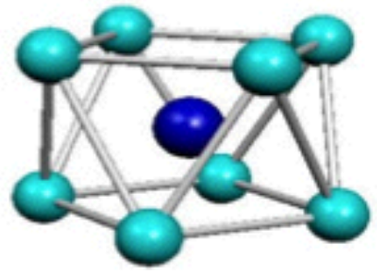
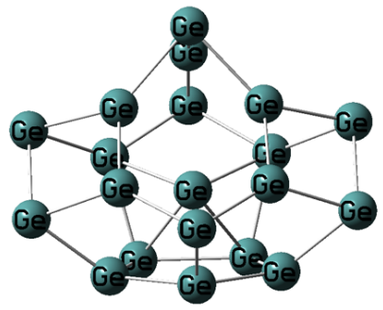
What are atomic clusters

- Atomic clusters are aggregates of atoms: `Molecules', but do not occur naturally
- Large size range: from a few to a few hundred/thousand atoms
- Can be `pure' or mixed (binary, ternary… clusters)
- Bridge between atoms and bulk: new `phase' of matter
- Extreme size dependence of properties
- Test bed for theories on finite systems
- Applications: catalysis, medical technology



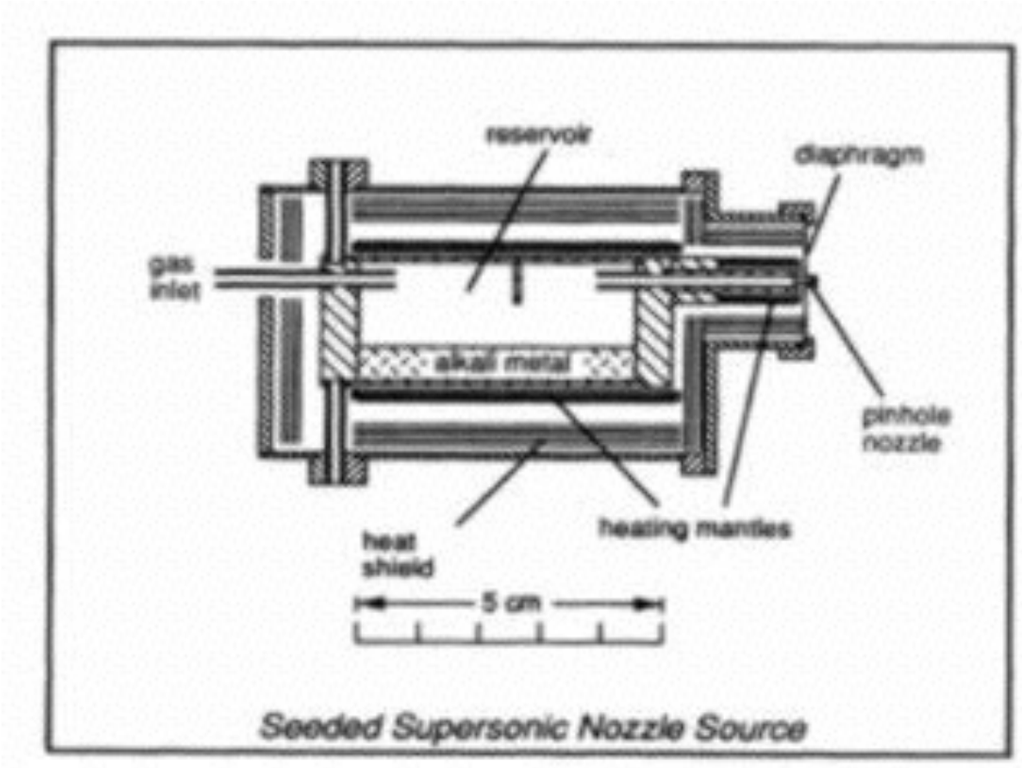
$FeCa_8$



Ge_{20}

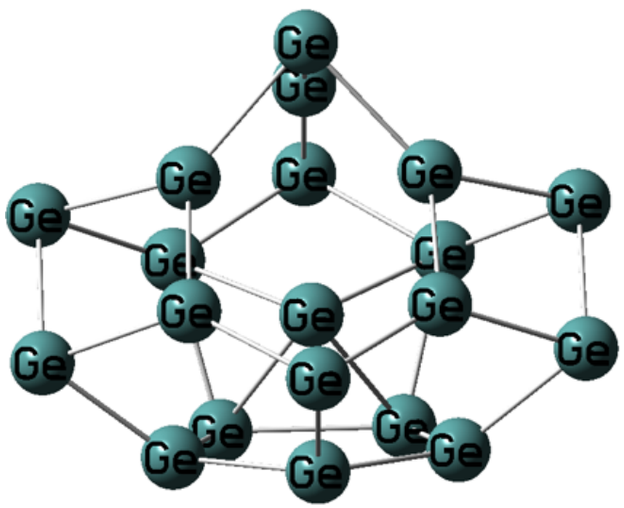
Structure, structure and structure …

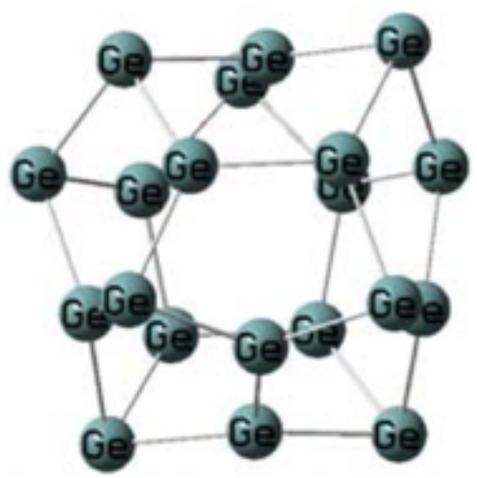
- Experimentalists can chose clusters of particular size (mass) using mass spectrometer/analyzer
  - Measure their properties
- How do we know how the atoms in a cluster are arranged, its structure?
  - For a few-atom cluster moving inside a flow tube, no experiments directly gives information of structure
  - Synergy of theory and experiment



Seeded Supersonic Nozzle Source

- Many possible **isomers** for a cluster of given size and composition





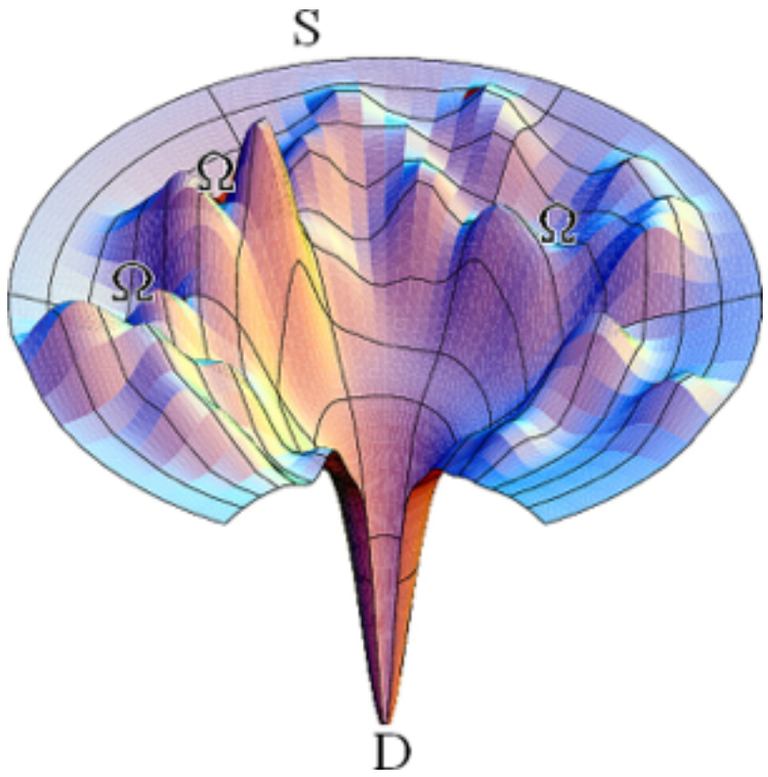
Two isomers of Ge_{20} Bandyopadhyay and Sen, JPCA 114, 1835

- Many such possibilities: We could calculate which one has the lowest energy, other properties, if we knew all the structures, but we don't …

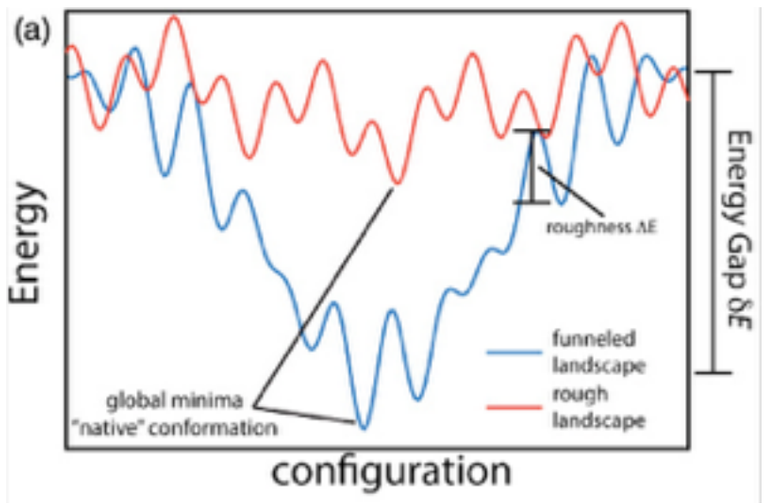
- How do we find the lowest (and may be a few higher) energy isomers without any direct input from experiments?

Some basics …

- We are interested in the internal (due to interaction between the atoms) energy of the cluster
- Kinetic energy of the CM and rotation of the cluster irrelevant
- Internal configuration space is (3N-6) dimensional
- We think in terms of the energy landscape in this space



Ω's local minima
meta-stable isomers
D global minimum



Simplified representation of the energy landscape

- How do we find this landscape, the global minimum? Exponential rise in number of local minima

- LJ clusters have ~1000 isomers for N=13, and ~10^{140} for N ~100!!!

Deaven et al, 1995

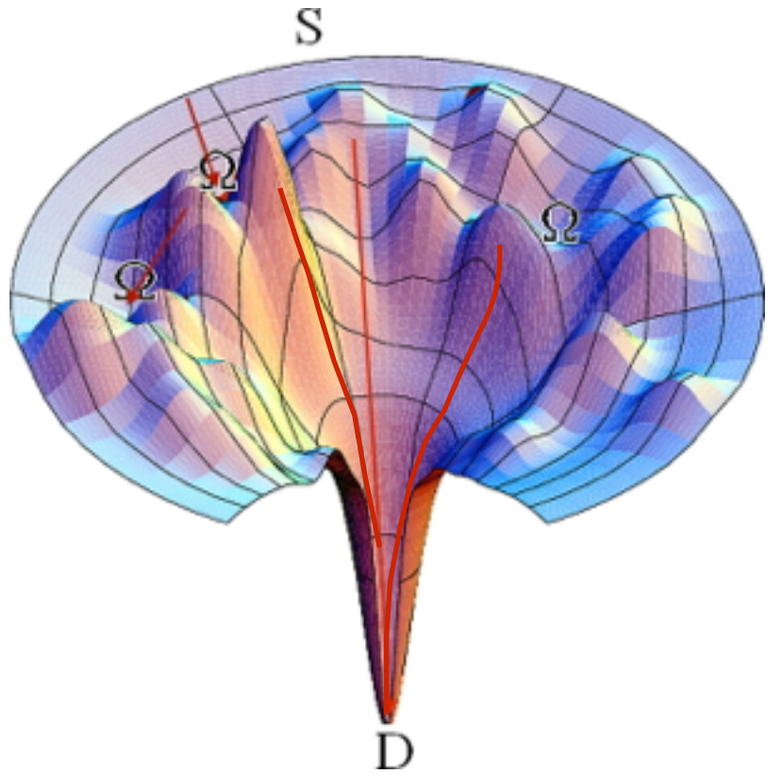
Strategies …

- Strategies based only on local optimization
  - Random search
  - Educated guess
  - Big bang
- Direct search for the global minimum
  - Genetic (evolutionary) algorithm
  - Basin hopping (+ occasional jumping)
  - Simulated annealing
  - Minima hopping

Local optimization

- Random search
  - Too many structures to be studied

Bad idea

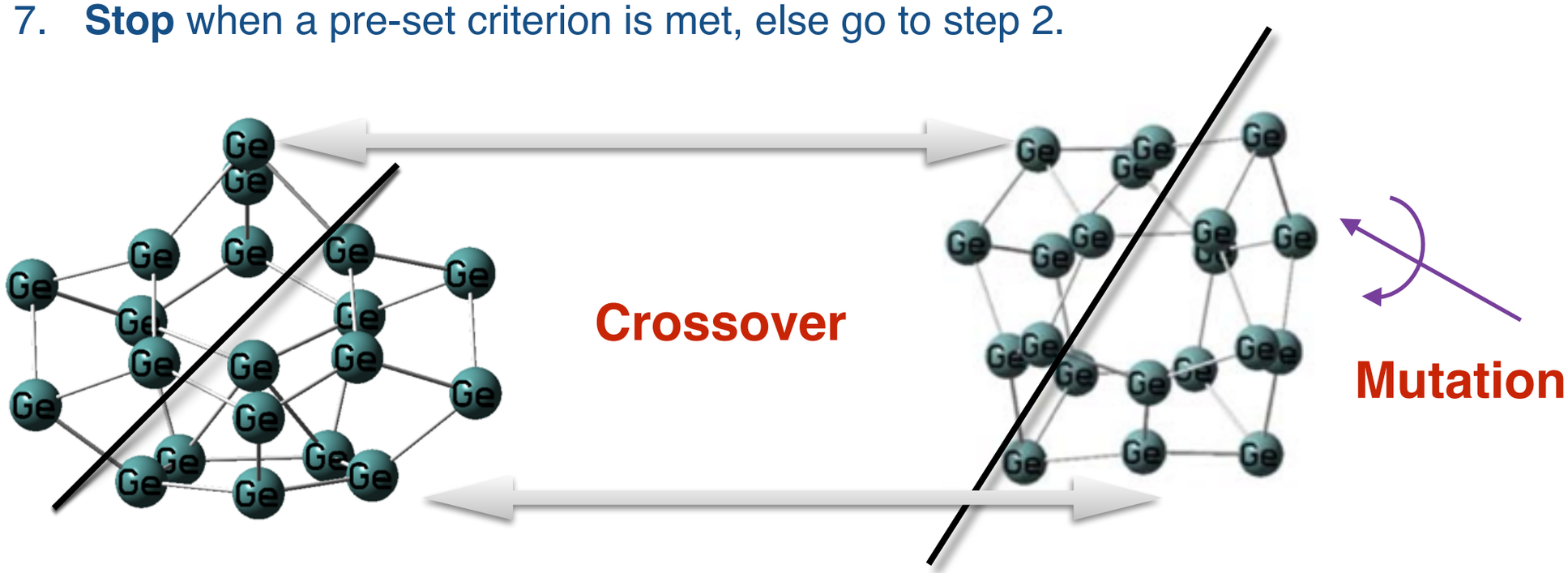


- Educated guess
  - Guess a few reasonable structures, relax (locally optimize) to the nearest local minimum
- Big Bang Jackson et al, Comp. Mat. Sc. 2006
  - Start from a few extremely compressed structures, relax them
  - Works very well for some inter-atomic potentials (LJ, e.g.), not always
  - Why does it work even for LJ? No idea !!!

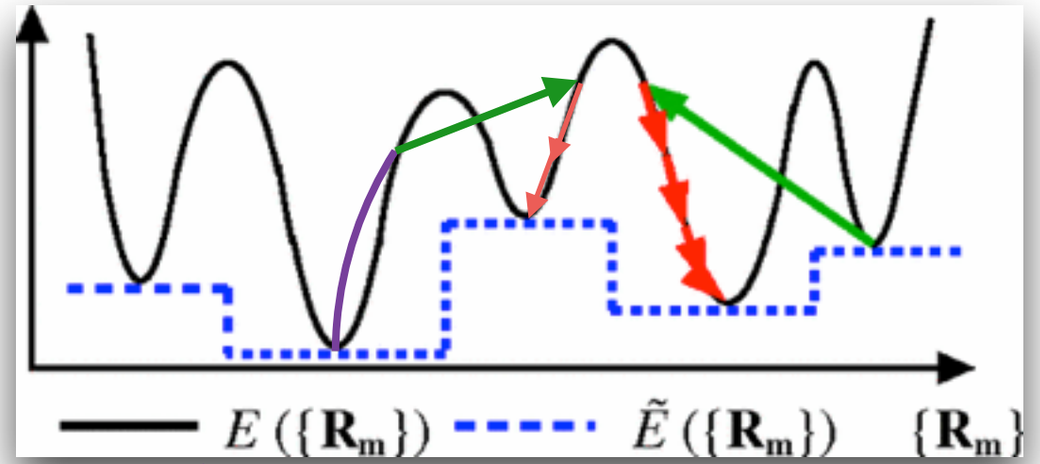
Direct search for the global minimum

- **GA**

1. Generate initial **Population:** Population a set of isomers
2. Assign **fitness** to each member based on energy: lower the energy, higher the fitness
3. Select two **parents** for crossover: higher the fitness, higher the probability of getting selected
4. Generate new **offspring**
5. Do a **mutation** with a small probability
6. Place the offspring in the new **population**
7. **Stop** when a pre-set criterion is met, else go to step 2.



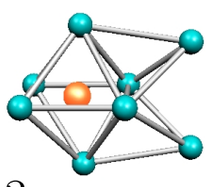
- **Basin hopping**
  - MC moves: usually simultaneous movement of all the atoms.
  - Local optimization is crucial
  - Accept with P=exp(-βΔE)

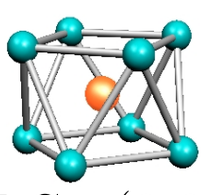


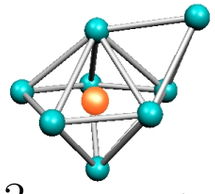
- Occasional jumping
  - When hopping fails for a certain number of attempts
  - Always accepted, no local min, effectively β~0, i.e., T~∞
  - Helps get out of traps

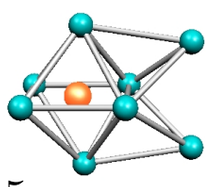
Application to real clusters …

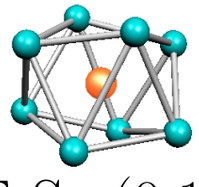
- TM-alkaline earth clusters clusters
  - $FeCa_8$ structures and spin states obtained using GA
  - Educated guess always produced the global minimum at this and similar sizes

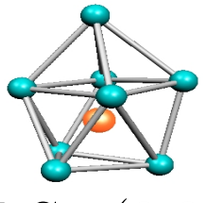

$^3FeSr_8(GS)$

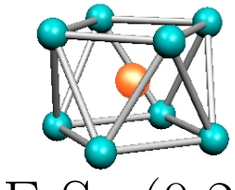

$^5FeSr_8(0.02eV)$

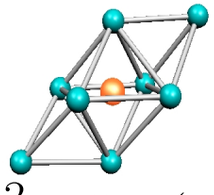

$^3FeSr_8(0.13eV)$

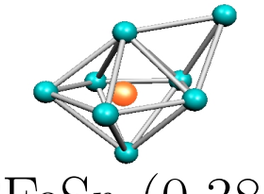

$^5FeSr_8(0.17eV)$

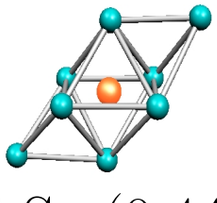

$^3FeSr_8(0.18eV)$


$^5FeSr_8(0.20eV)$


$^3FeSr_8(0.25eV)$


$^3FeSr_8(0.37eV)$

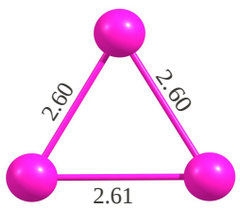

$^5FeSr_8(0.38eV)$


$^5FeSr_8(0.44eV)$

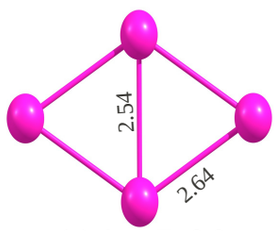
Chauhan and Sen, Chem. Phys. 2013

and Ag clusters …

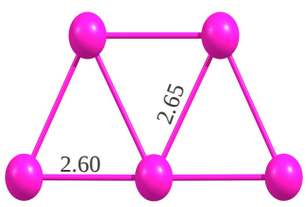
(a) Ag_2, E=0.0



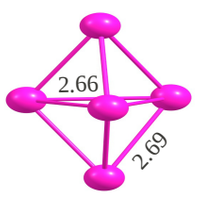
(b) Ag_3, E=0.0



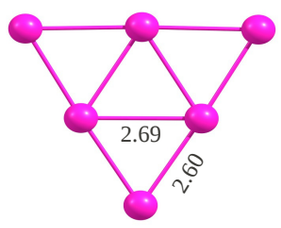
(c) Ag_4, E=0.0



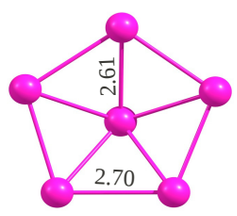
(d) Ag_5, E=0.0



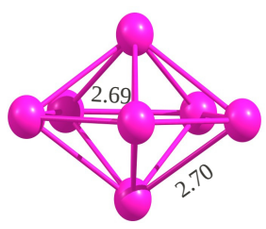
(e) Ag_5, E=0.38



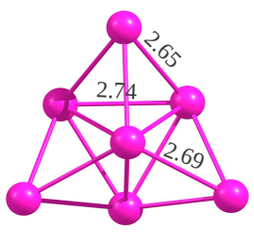
(f) Ag_6, E=0.0



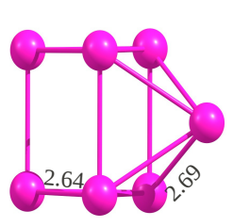
(g) Ag_6, E=0.12



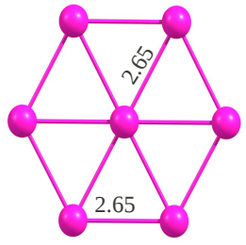
(h) Ag_7, E=0.0



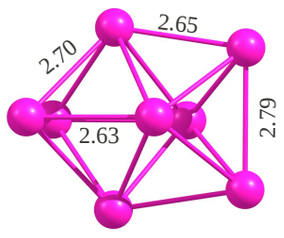
(i) Ag_7, E=0.23



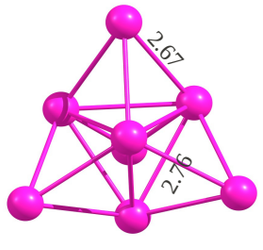
(j) Ag_7, E=0.41



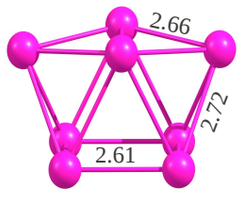
(k) Ag_7, E=0.81



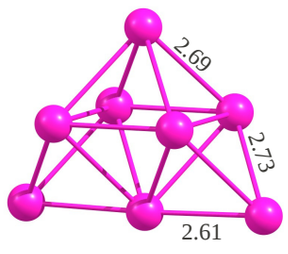
(l) Ag_8, E=0.00



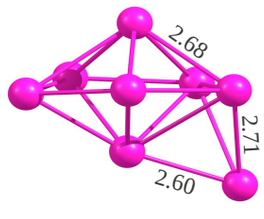
(m) Ag_8, E=0.07



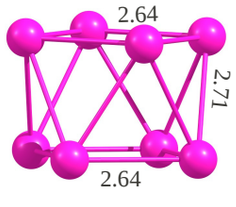
(n) Ag_8, E=0.17



(o) Ag_8, E=0.19



(p) Ag_8, E=0.19

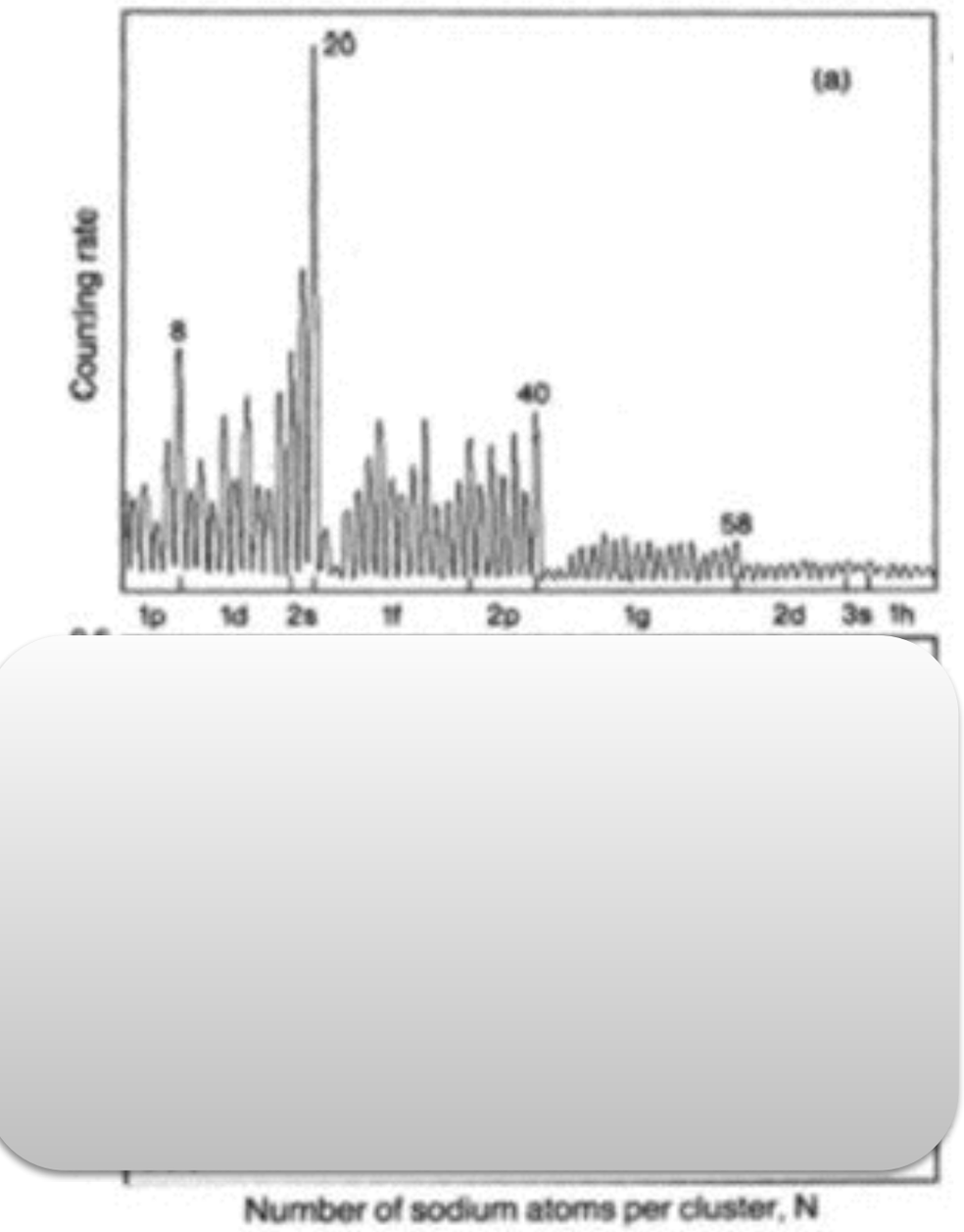


(q) Ag_8, E=0.33

Singh, and Sen, JCP, 2014

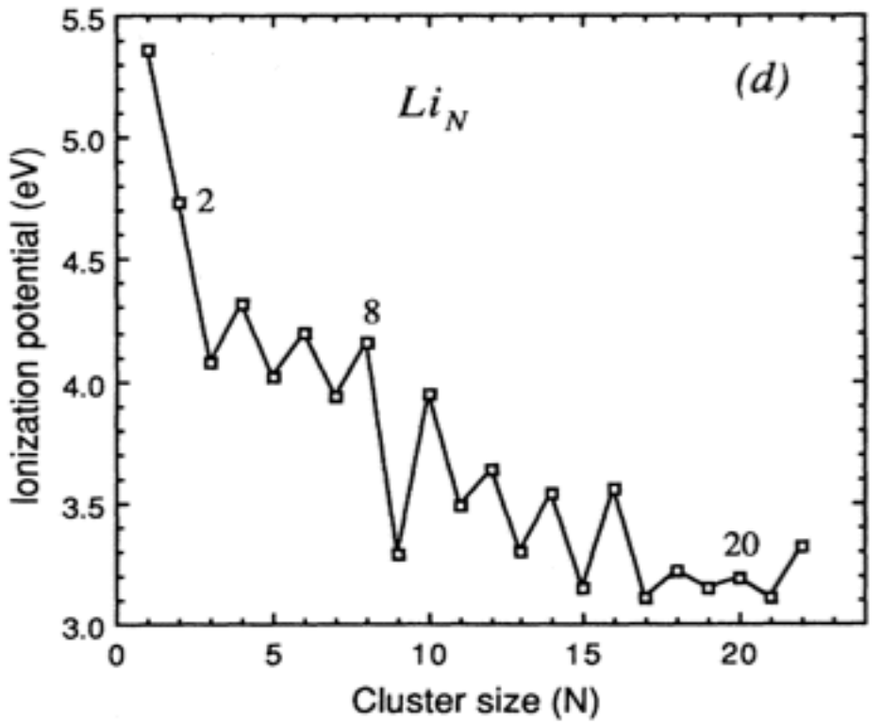
What's interesting about these clusters?

- Experiments …
  - Greater abundance at certain sizes, electron numbers



Knight et al, PRL 1984

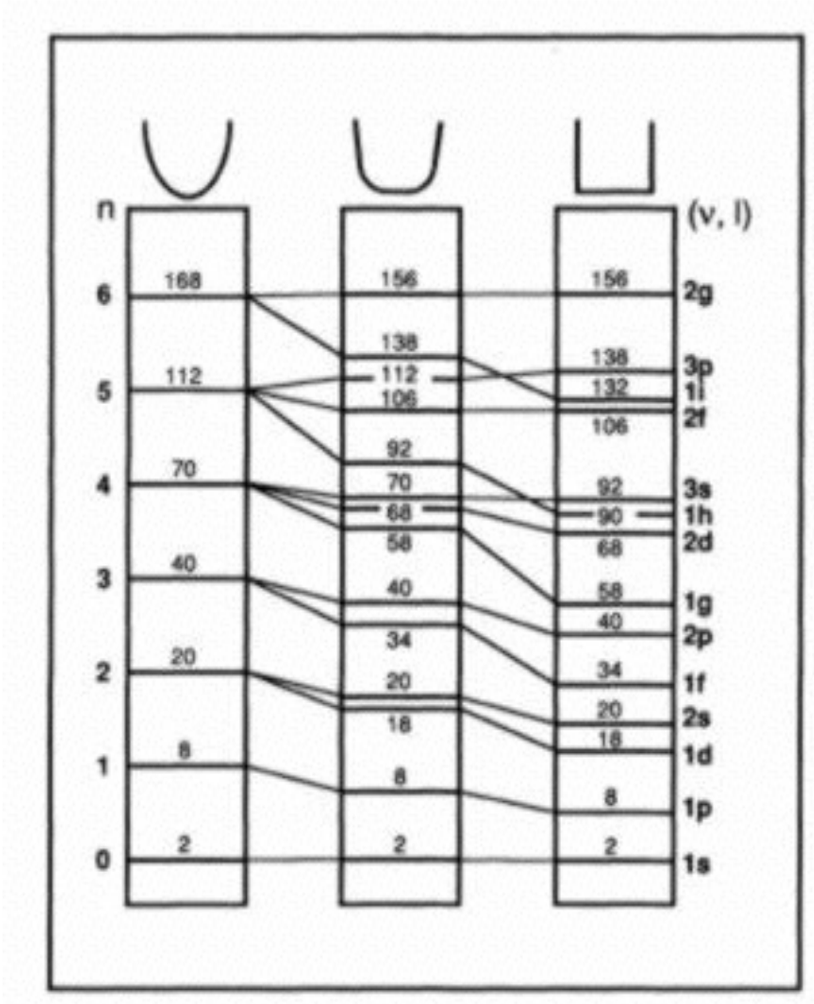
- Drop in IP as a new shell starts getting filled



Dugourd et al, 1992

How do we rationalise these?

- Shell models for metal clusters
  - Valence electrons move freely in the region of confinement
  - Quantum confinement leads to discrete energy states
  - Symmetry leads to degeneracy
  - Spherical models explain many features of simple metal clusters



Stability measured theoretically by some of the following quantities

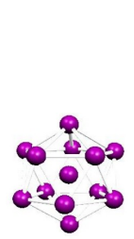
1. HOMO-LUMO gap
2. Chemical hardness

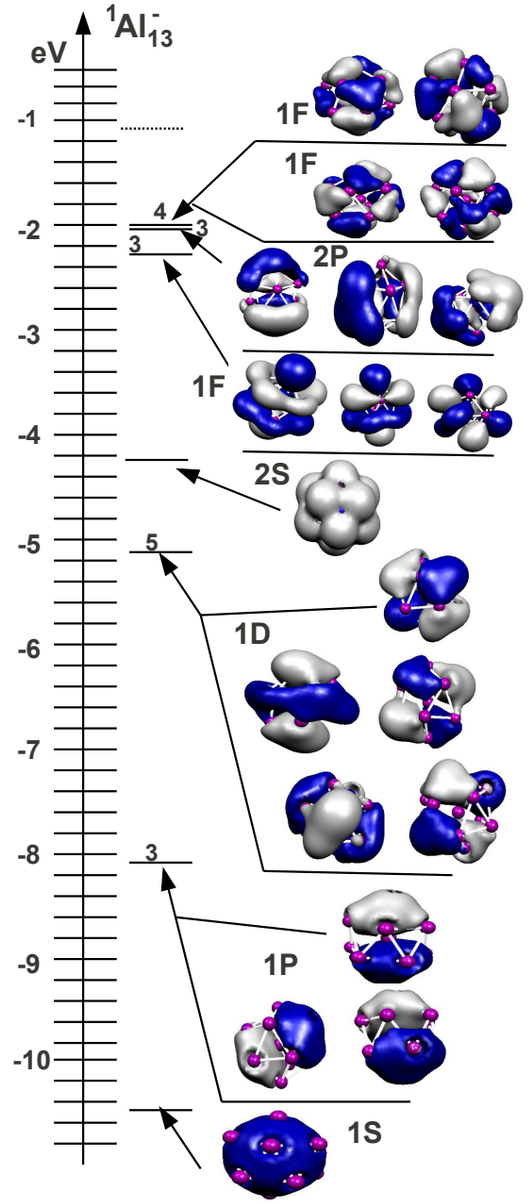
$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right) \approx \frac{\mathrm{IP} - \mathrm{EA}}{2}$$

3. $\Delta = E(n-1) - E(n)$
4. $\Delta^2 = E(n+1) + E(n-1) - 2E(n)$
5. $\Delta E_{spin} = E(\text{1st spin excited state}) - E(\text{g.s.})$

Two questions …

- Do the MO's in real clusters really look like S, P, D, …-like orbitals in atoms?
- How far can this analogy be stretched?





$1S^21P^61D^{10}2S^21F^{14}2P^6$

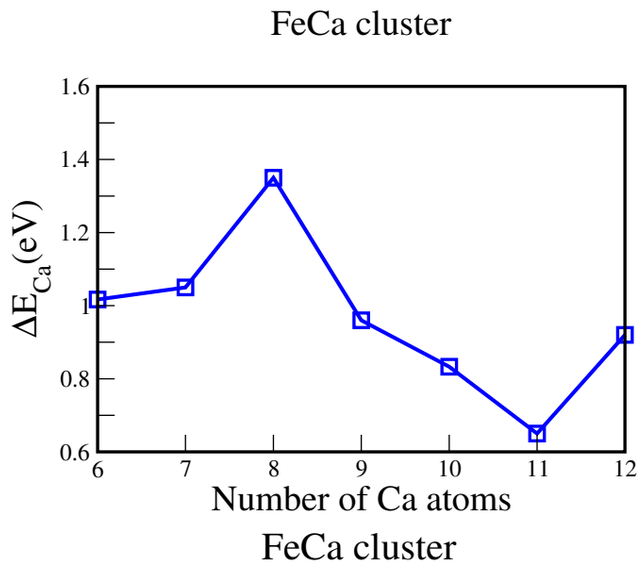
- Clusters as superatoms
- Al_{13} as halogen, EA =3.4 eV
- Al^-_{13} as inert gas atoms

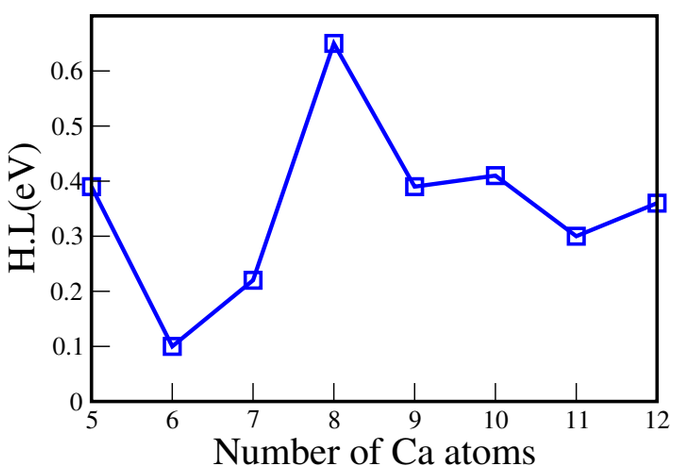
Clusters that behave as atoms
retain their structure in assemblies
termed **superatoms**

Stability measured theoretically by some of the following quantities

1. HOMO-LUMO gap
2. Chemical hardness $\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right) \approx \frac{\mathrm{IP} - \mathrm{EA}}{2}$
3. $\Delta E = E(n-1) - E(n)$
4. $\Delta^2 = E(n+1) + E(n-1) - 2E(n)$
5. ΔE_{spin} = E(1st spin excited state) - E(g.s.)

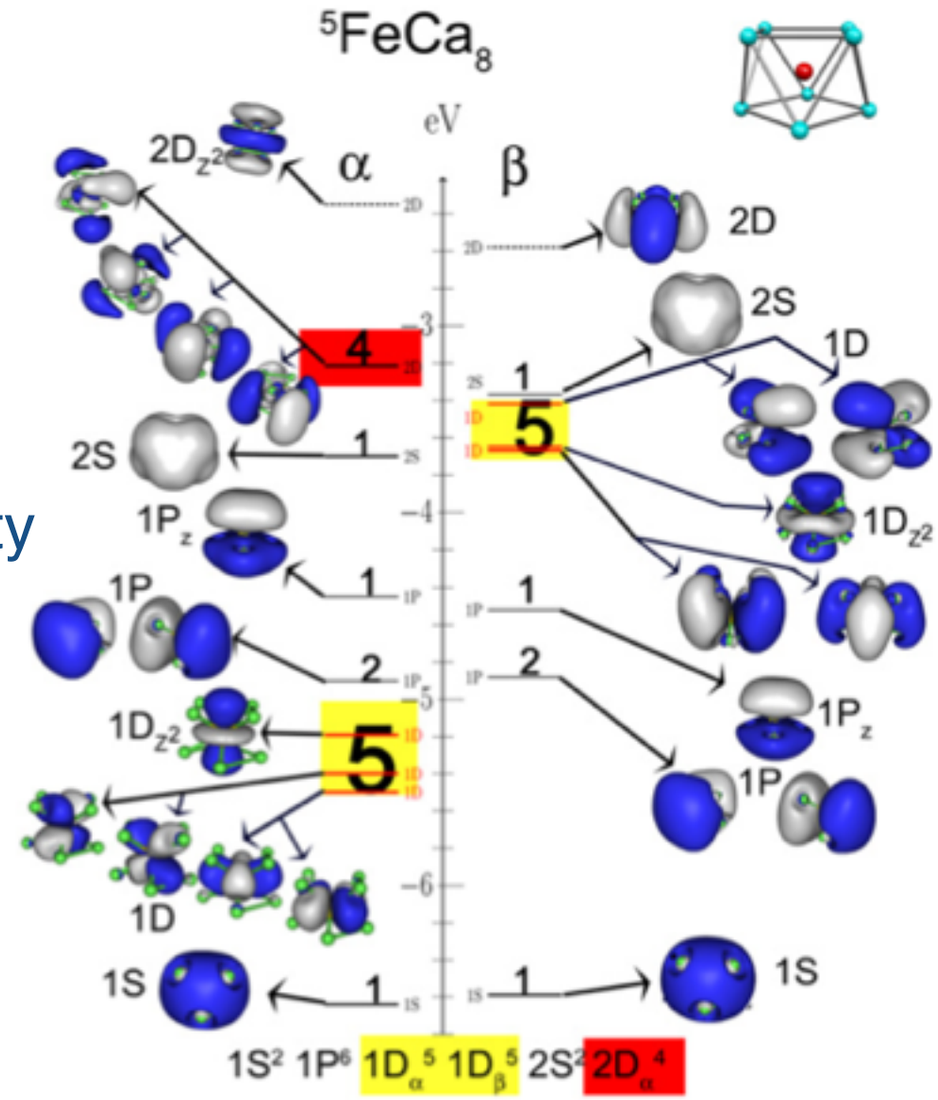
TM-Ca/Sr clusters as superatoms but magnetic





Why enhanced stability at 24 valence electrons?

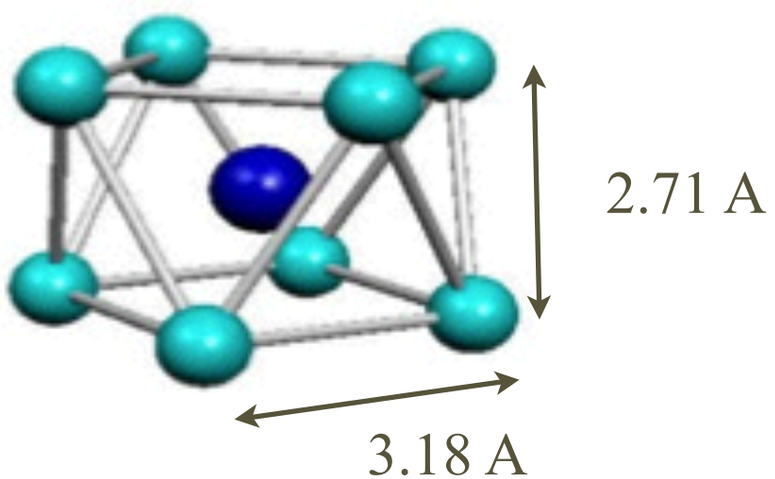
$FeCa_8$ has enhanced stability



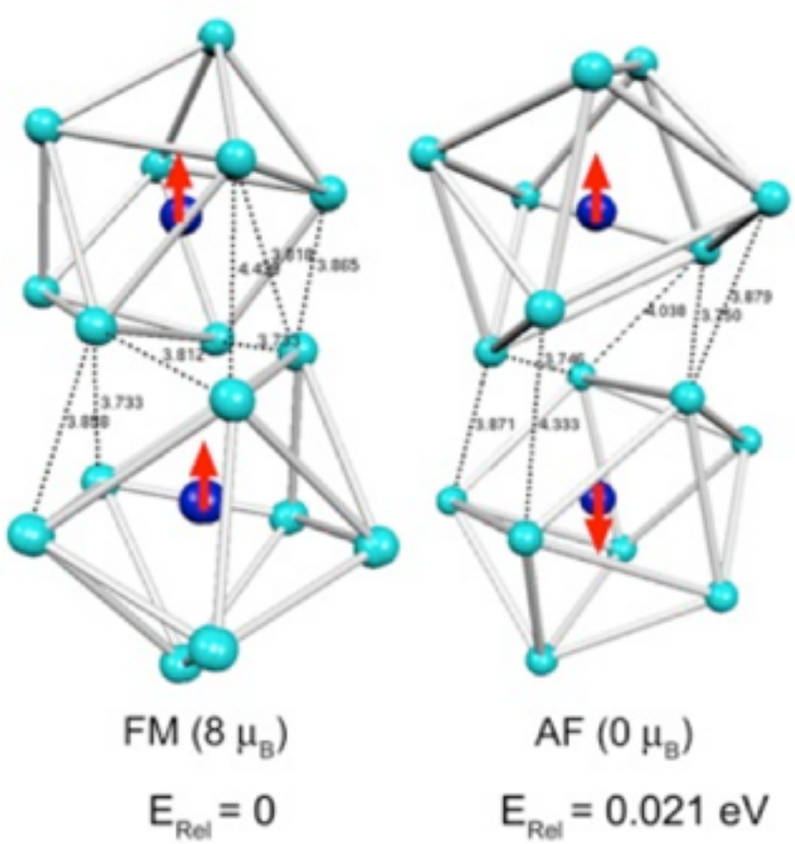
Three important points

1. 2D orbitals before 1F
2. `Crystal field' splitting
3. Hund's rule in shell orbitals

- **Crystal field effect**
  - An `oblate spheroid' shape for $FeCa_8$
  - P_z and D_{z^2} orbitals are pushed up in energy
- **Hund's coupling** or exchange splitting in 2D orbitals
- **Interplay** of these give sub-shell filling at 24 valence electrons &
  - Magnetic moment 4 μ_B



Assemblies of $FeCa_8$

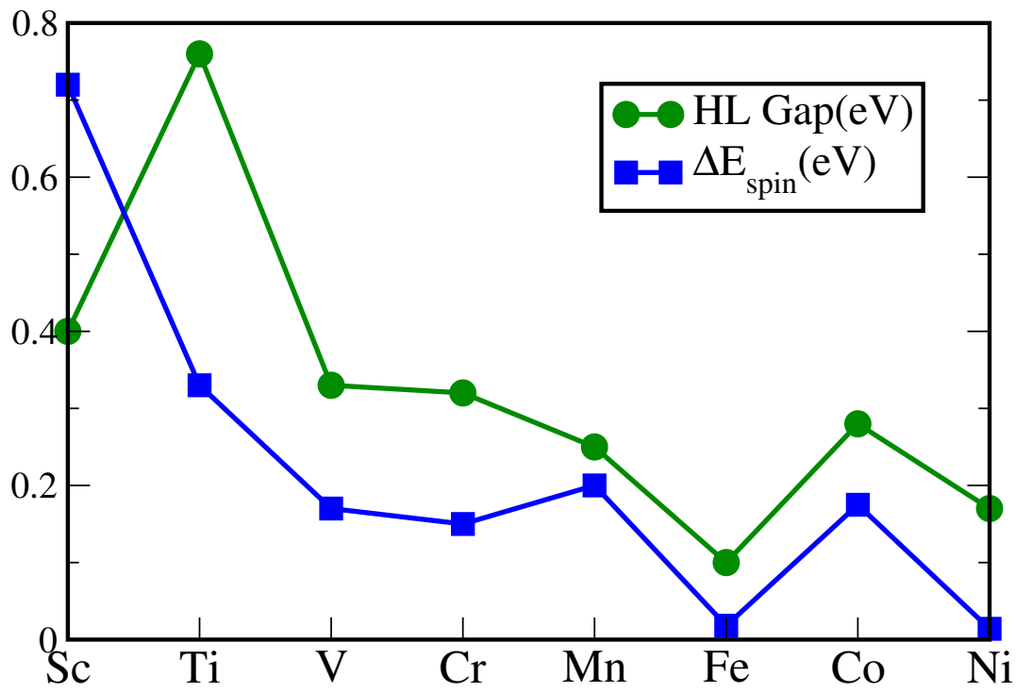


Stable dimer

$FeCa_8$ as a magnetic superatom

Chauhan et al, CPL 2013

Identifying stable $TMSr_8$ clusters



$TiSr_8$ has the largest HOMO-LUMOL gap and chemical hardness
20-electron filled shell

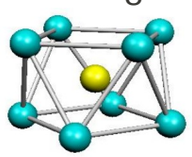
$CoSr_8$ has a small peak locally

Cluster	M=2S+1	Hardness (η)	
		ΔSCF	Koopmans' theorem
ScSr	2	1.35	0.23
TiSr	**1**	**1.45**	**0.38**
VSr	2	1.36	0.17
CrSr	3	1.26	0.16
MnSr	4	1.23	0.13
FeSr	3	1.2	0.05
CoSr	2	1.26	0.14
NiSr	3	1.2	0.09

No promising candidates for magnetic superatoms

Why is $FeSr_8$ not special? Structure …

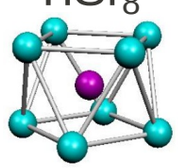
$^{2}ScSr_8$



$r_{Sc-Sr} = 3.46$

$r_{Sr-Sr} = 4.21$

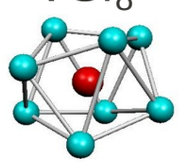
$^{1}TiSr_8$



$r_{Ti-Sr} = 3.33$

$r_{Sr-Sr} = 4.00$

$^{2}VSr_8$



$r_{V-Sr} = 3.28$

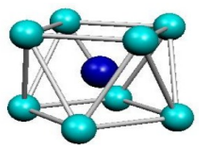
$r_{Sr-Sr} = 3.95$

$^{3}CrSr_8$

$r_{Cr-Sr} = 3.31$

$r_{Sr-Sr} = 3.92$

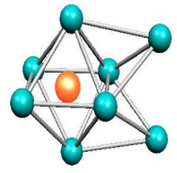
$^{4}MnSr_8$



$r_{Mn-Sr} = 3.30$

$r_{Sr-Sr} = 3.95$

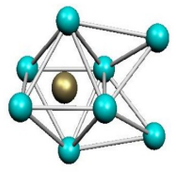
$^{3}FeSr_8$



$r_{Fe-Sr} = 2.92$

$r_{Sr-Sr} = 4.14$

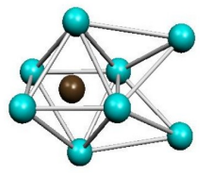
$^{2}CoSr_8$



$r_{Co-Sr} = 2.86$

$r_{Sr-Sr} = 4.01$

$^{3}NiSr_8$



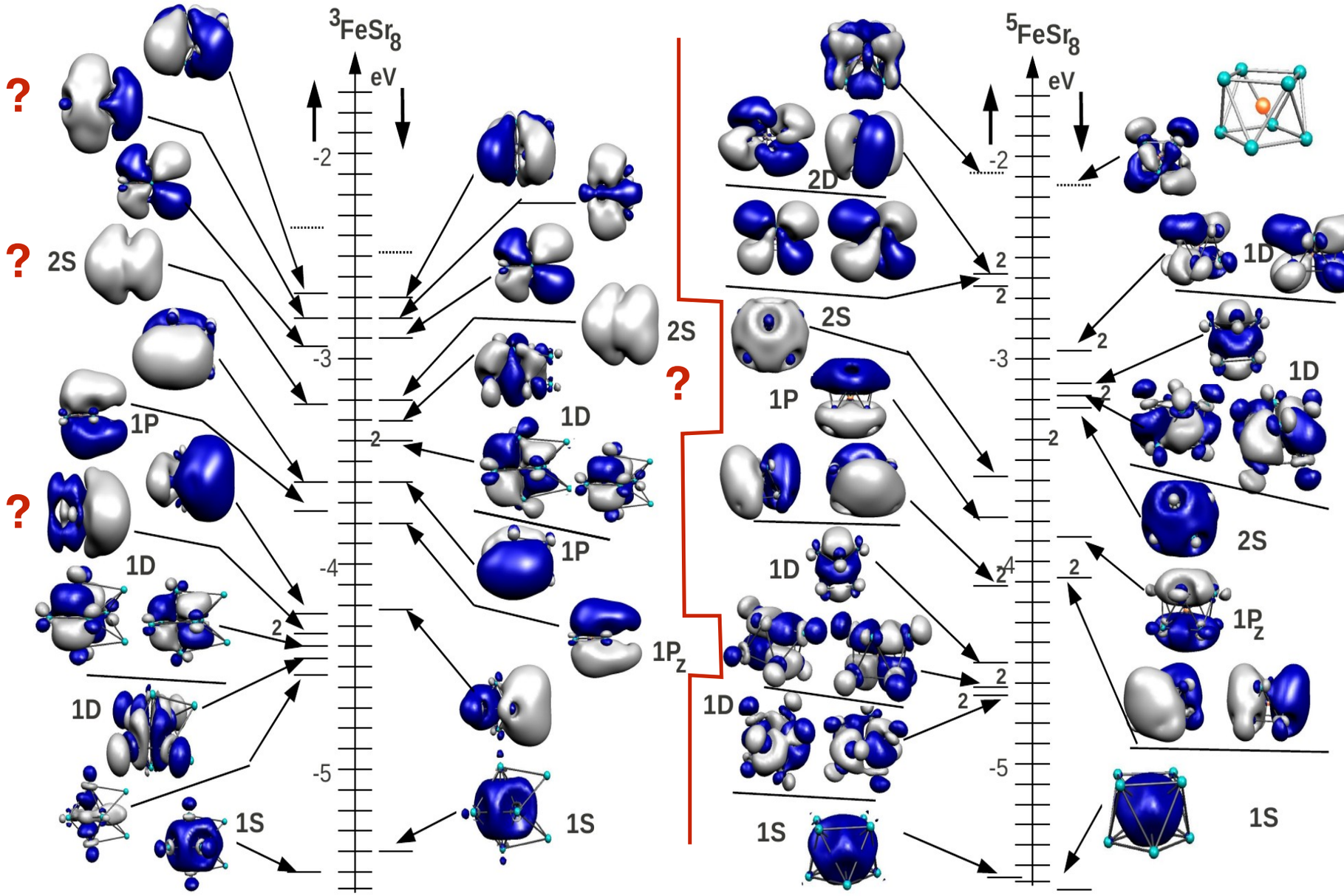
$r_{Ni-Sr} = 2.90$

$r_{Sr-Sr} = 4.03$

GS structures of $TMSr_8$ clusters

Structure and electronic shells

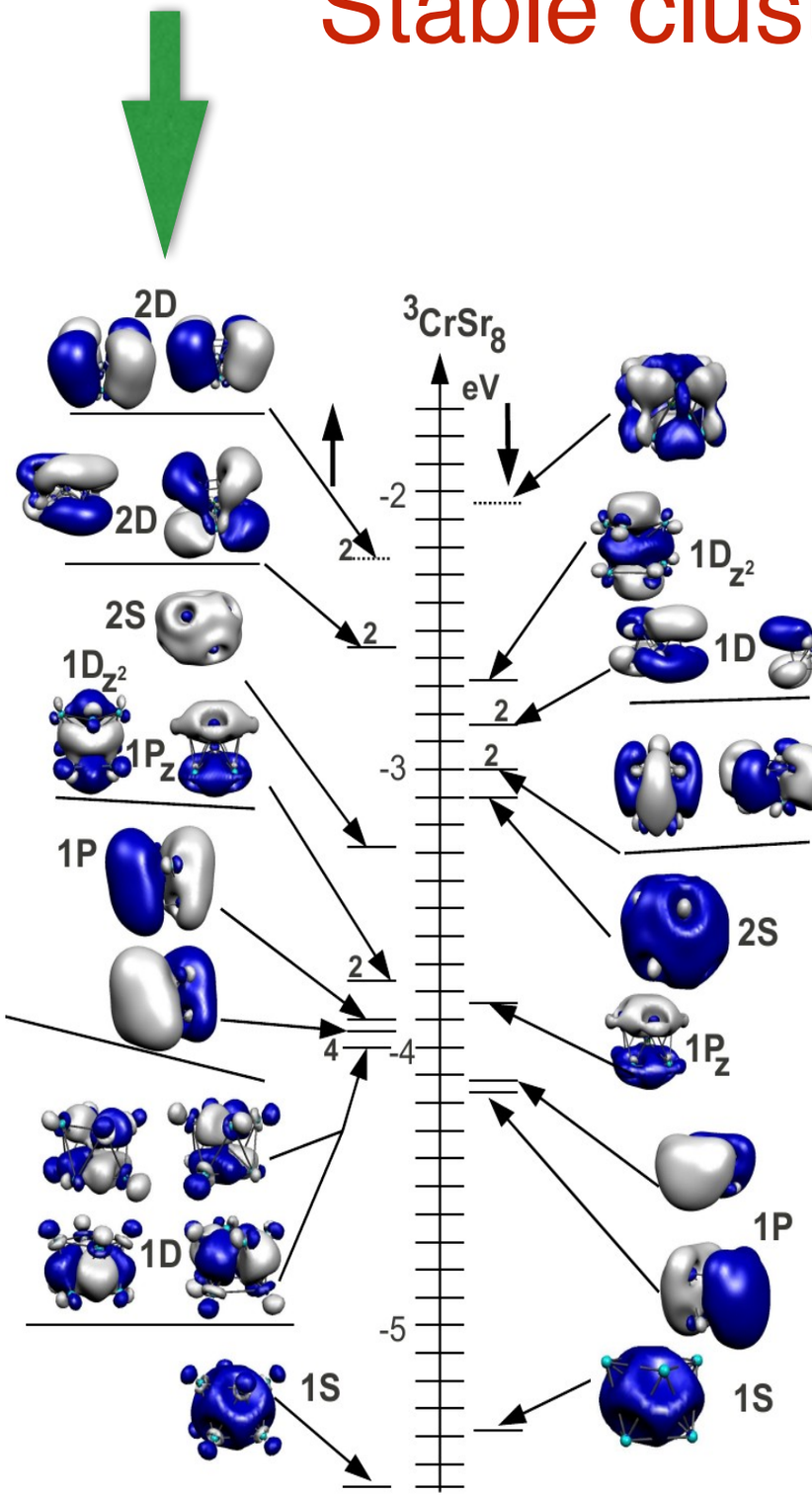
$1S^2 1P^6 1D^{10} 2S^2 2D_\alpha^4$



Non-compact low symmetry structure
Poor resemblance to shell orbitals

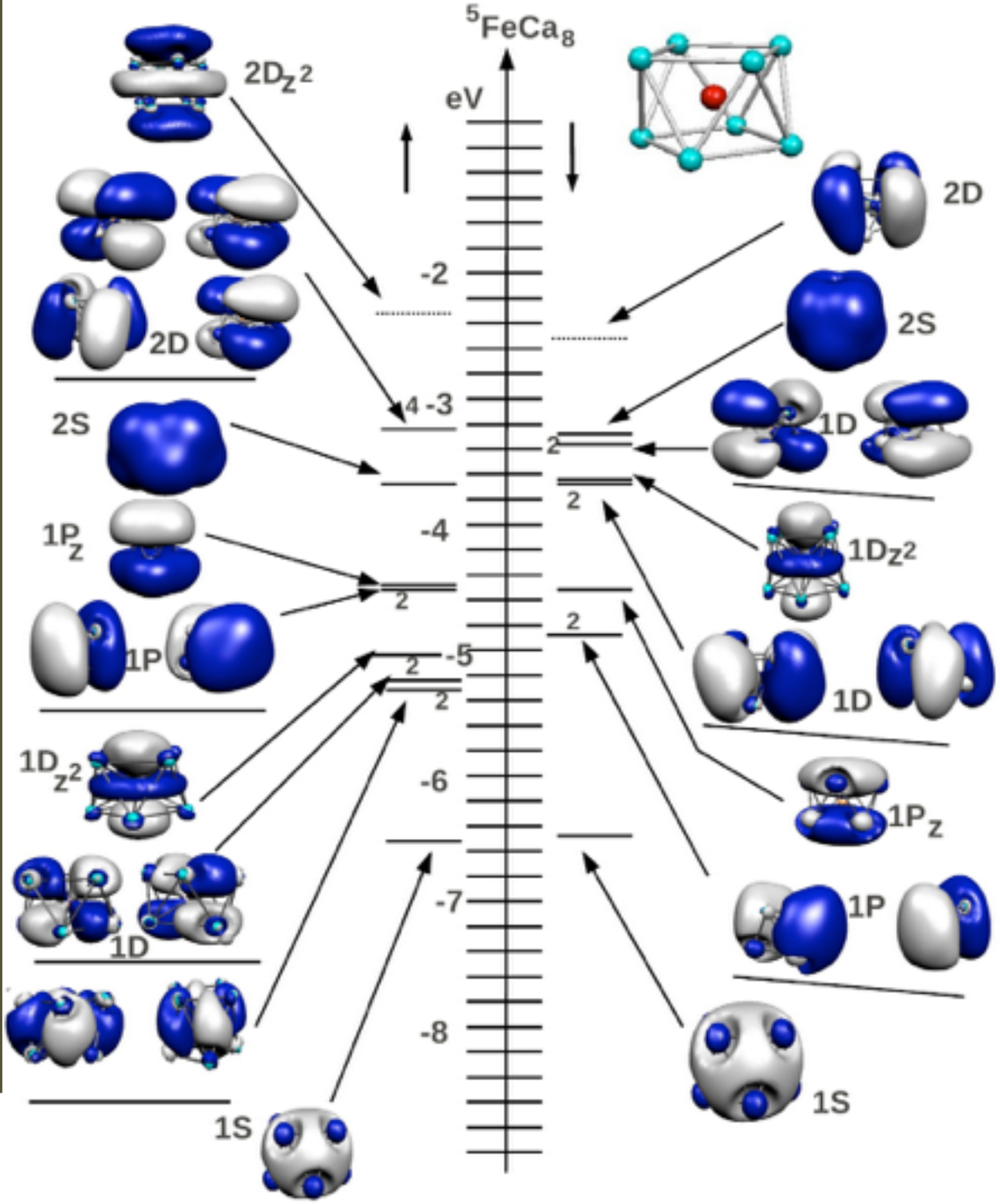
Compact high symmetry structure
Better resemblance to shell orbitals
Same electronic structure as $FeCa_8$

Stable clusters at other sizes in $TMSr_n$?



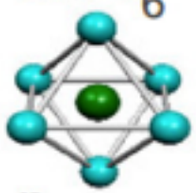
$1S^21P^61D^{10}2S^22D_\alpha^2$

$1S^21P^61D^{10}2S^22D_\alpha^4$



Relative stability of Cr-Sr clusters

$^3CrSr_6$



$r_{Cr-Sr=3.20}$

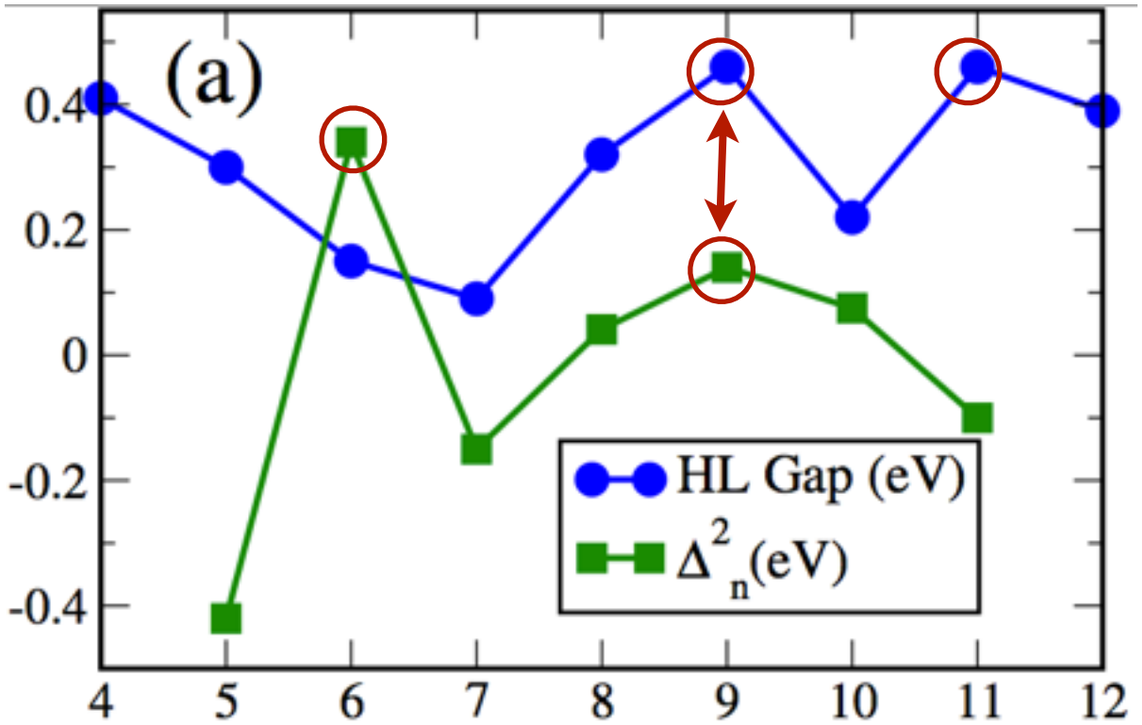
$r_{Sr-Sr=3.83}$

$^5CrSr_9$

$r_{Cr-Sr} = 3.42$

$r_{Sr-Sr=4.17}$

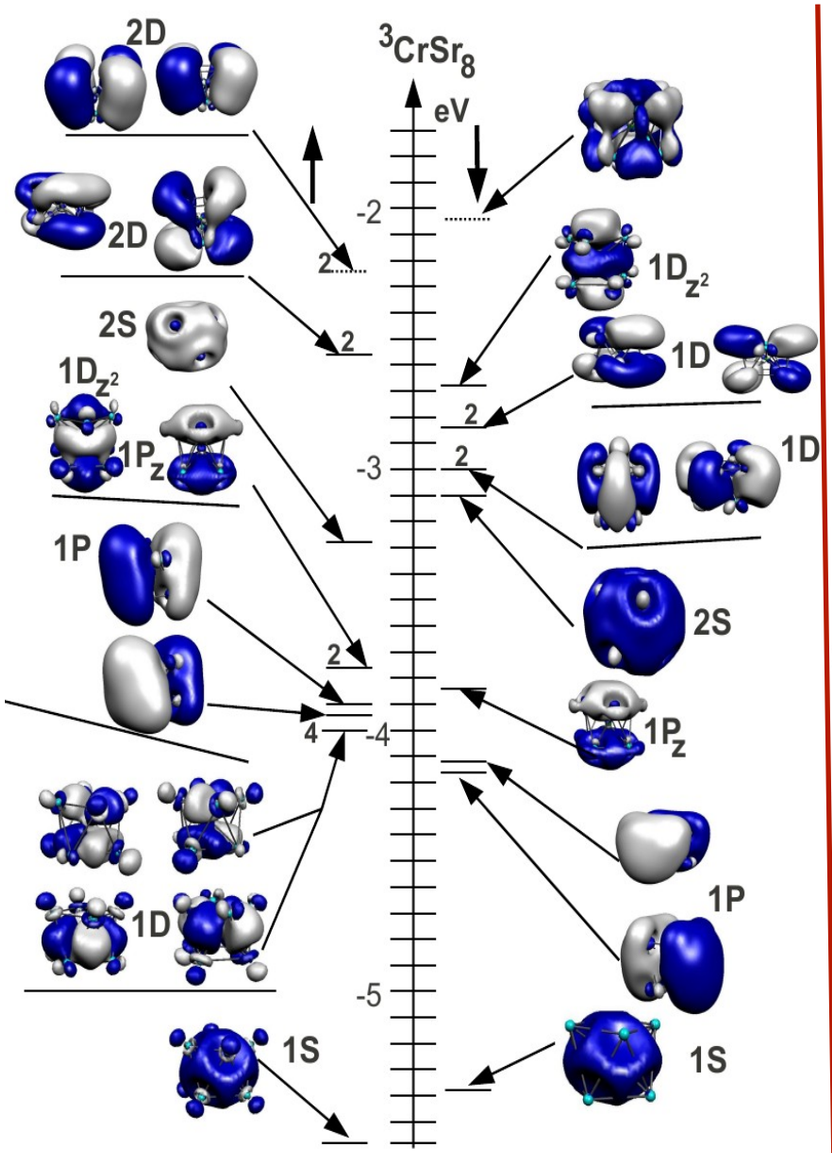
$r_z = 6.36$



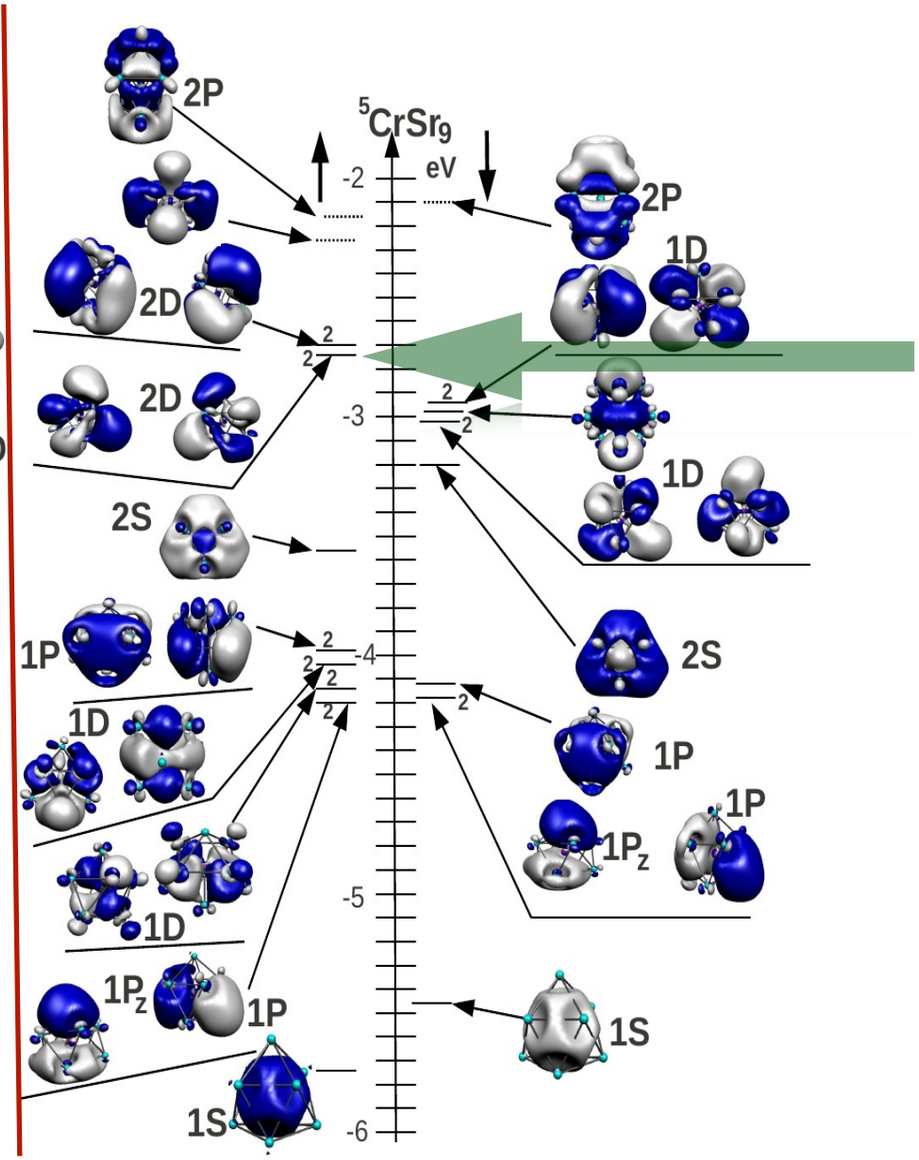
Cluster	M=2S+1	Hardness
CrSr	5	1.5
CrSr	5	1.41
CrCr	3	1.26
CrSr	3	1.21
CrSr	3	1.26
CrSr	**5**	**1.3**
CrSr	5	1.18
CrSr	3	1.29
CrSr	5	1.19

- Peaks in Δ^2 for $CrSr_6$ and $CrSr_9$
  - $CrSr_6$ compact octahedron
- Peaks in HOMO-LUMO gap and Δ^2 only in $CrSr_9$
- $CrSr_9$: enhanced stability due to sub-shell filling

What leads to sub-shell filling in $CrSr_9$?



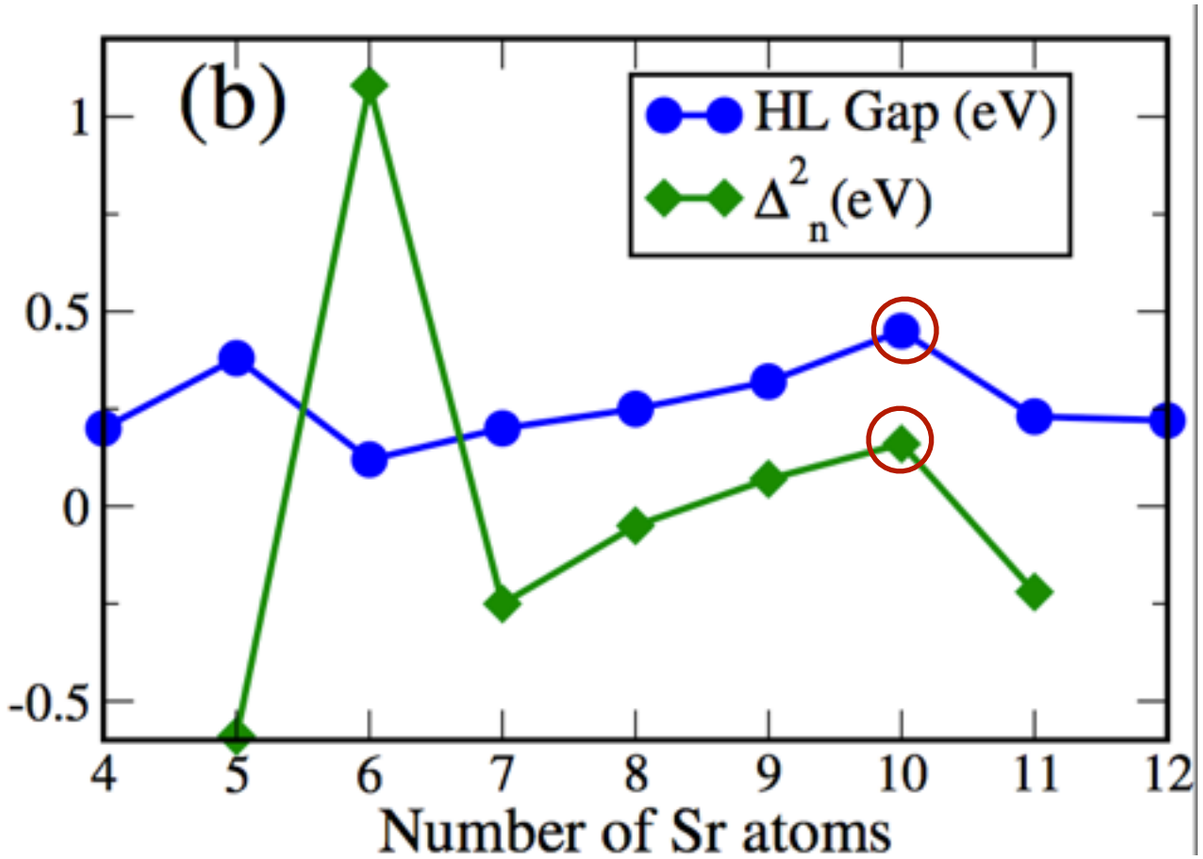
$1S^21P^61D^{10}2S^22D_\alpha^2$



$1S^21P^61D^{10}2S^22D_\alpha^4$

- Two electrons from the last Sr atom go into the $2D_\alpha$ orbital as anticipated
  - The last 2D orbital split to higher energy due to crystal field effect, large gap
- Exchange splitting leads to a $1S^21P^61D^{10}2S^22D_\alpha^4$ configuration, moment of 4 μ_B

Mn-Sr clusters …

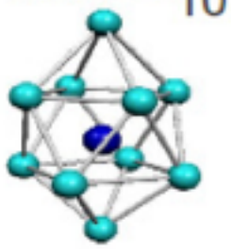


Cluster	M=2S+1	Hardness
MnSr	4	1.52
MnSr	4	1.43
MnCr	2	1.36
MnSr	2	1.34
MnSr	4	1.23
MnSr	6	1.25
MnSr	**6**	**1.34**
MnSr	4	1.1
MnSr	4	1.1

- $MnSr_6$ has a compact octahedron structure
- $MnSr_{10}$ has 27 valence electrons !!
  - Sub-shell filling? How?

Structure again …

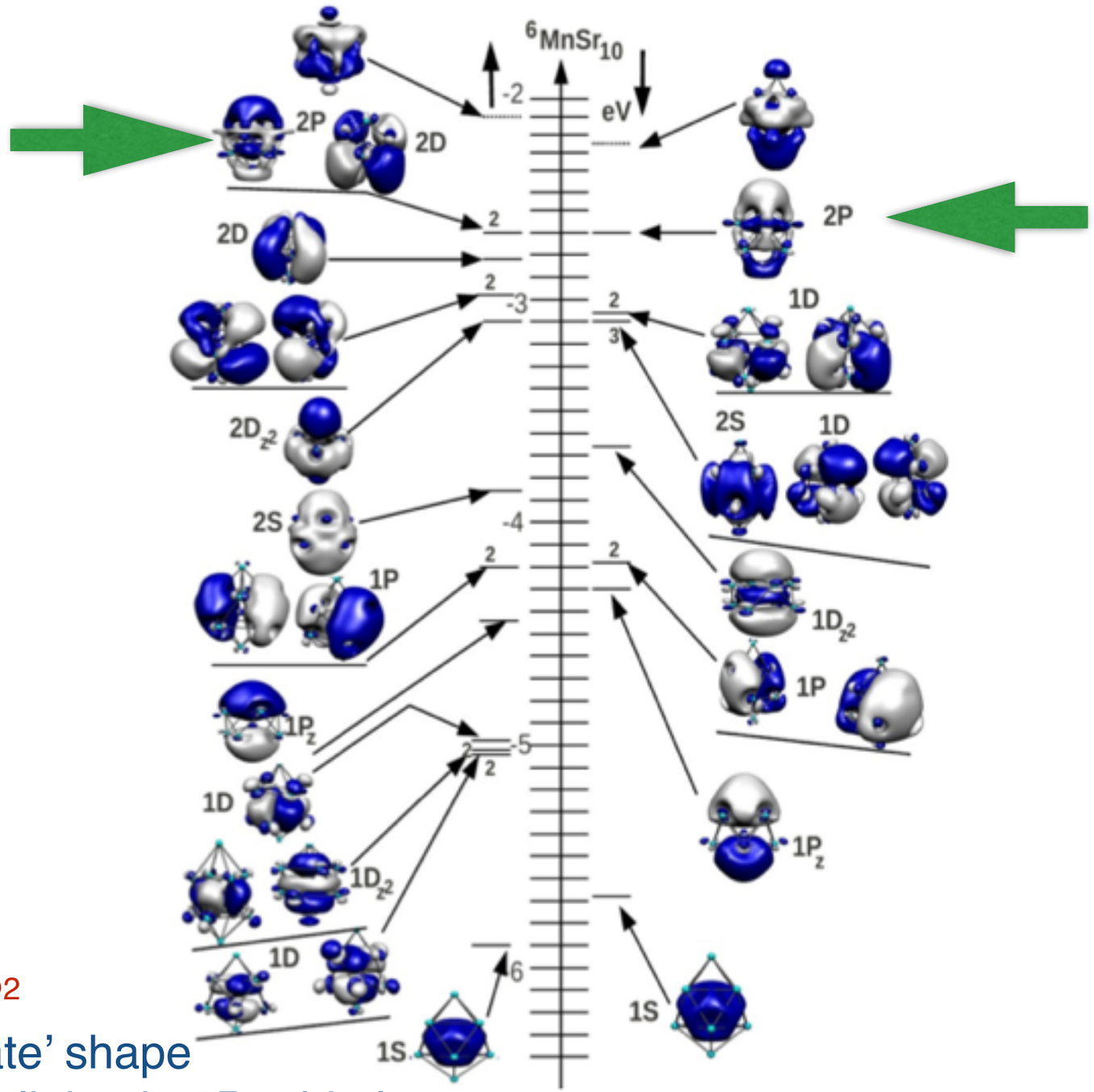
$^6MnSr_{10}$



$r_{Mn\text{-}Sr} = 3.38$

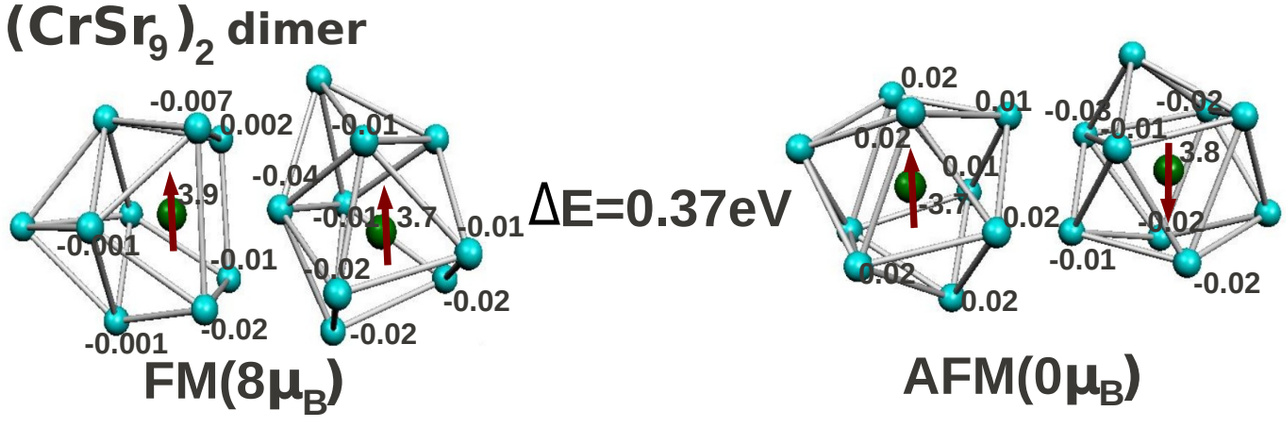
$r_{Sr\text{-}Sr} = 4.13$

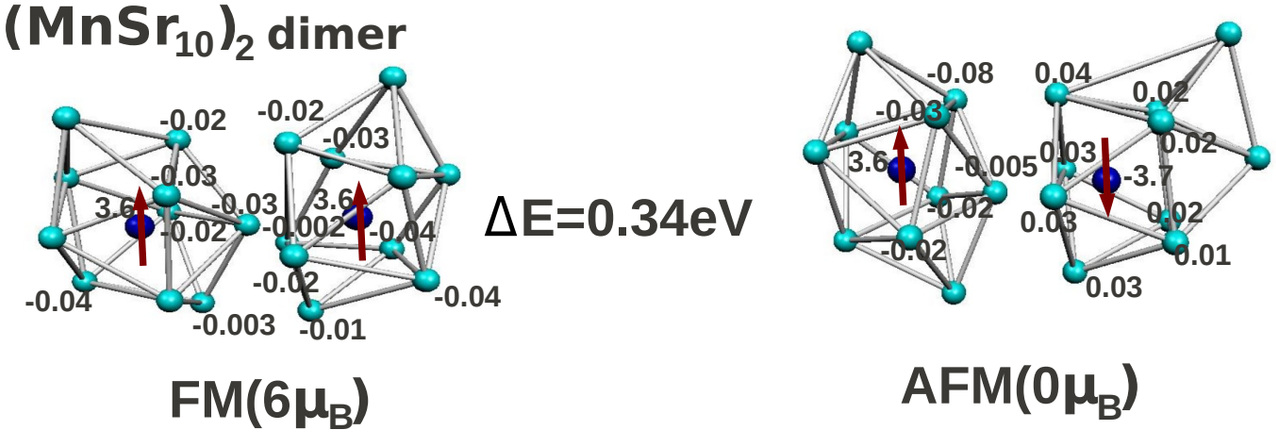
$r_z = 9.09$



- $MnSr_{10}$ has $1S^2 1P^6 1D^{10} 2S^2 2D_\alpha^5 2P^2$
- $2P_z$ orbitals stabilized due to `prolate' shape
  - Large gap due to crystal field splitting in 2P orbitals

Assemblies





- Studied both parallel and anti-parallel arrangements of spins
- Parallel alignment more stable on both cases

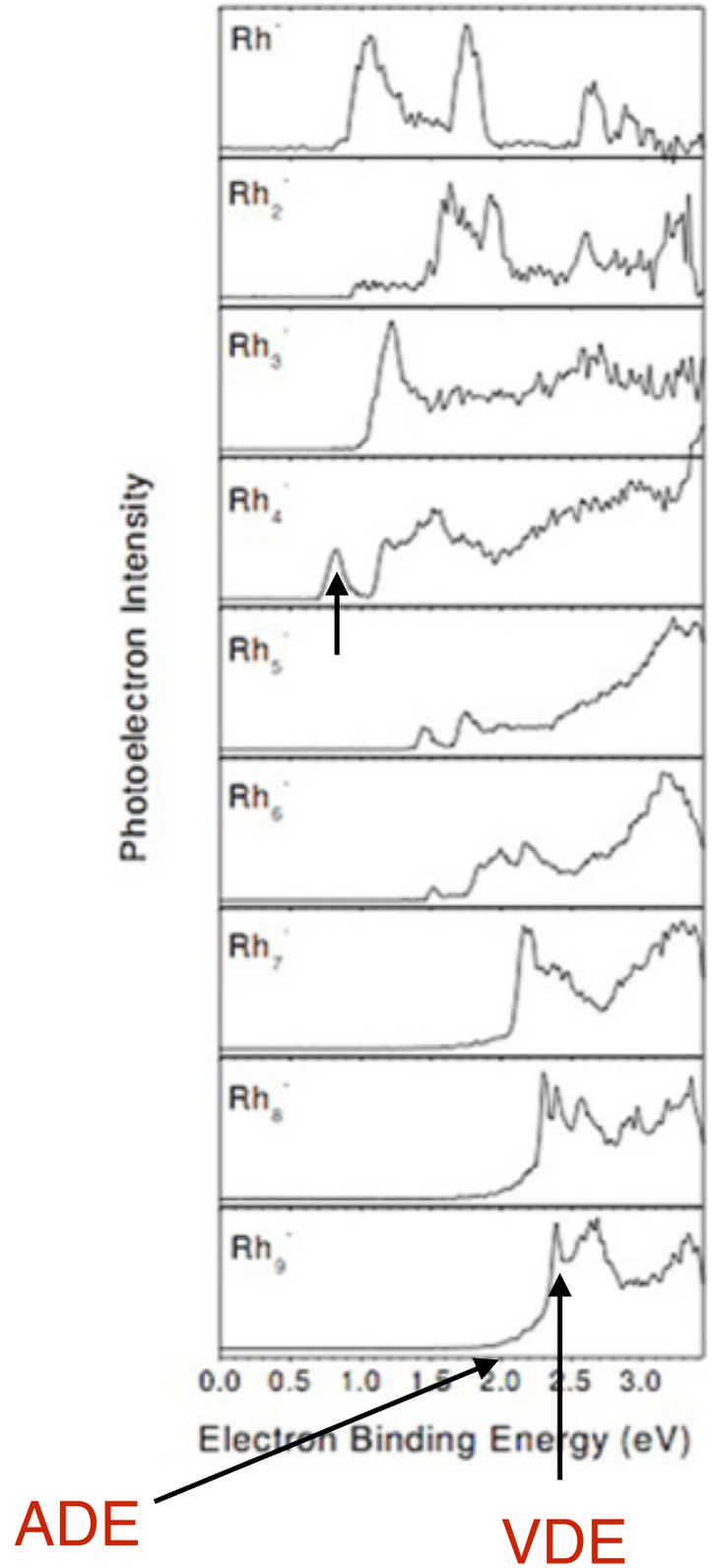
Chauhan and Sen, Chem. Phys. 2013

$CrSr_9$ and $MnSr_{10}$ are magnetic superatoms

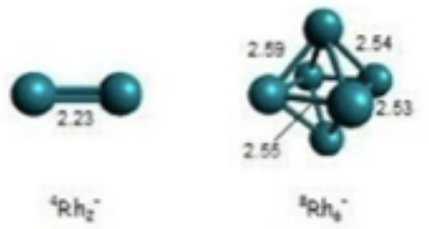
Theory-experiment synergy

- Small Rh_n clusters, shell models do not work
  - Magnetic, though the bulk is non-magnetic
  - Multiplicity of structure and magnetic states, difficult to find the global minimum
- Anion photoelectron spectra (PES)
  - EBE = hv - EKE
- Theory has to step in to suggest possible structures

$VDE = Rh^0_n(\text{anion geom}) - Rh^-_n(\text{anion geom})$
$ADE = Rh^0_n(\text{neutral geom}) - Rh^-_n(\text{anion geom})$

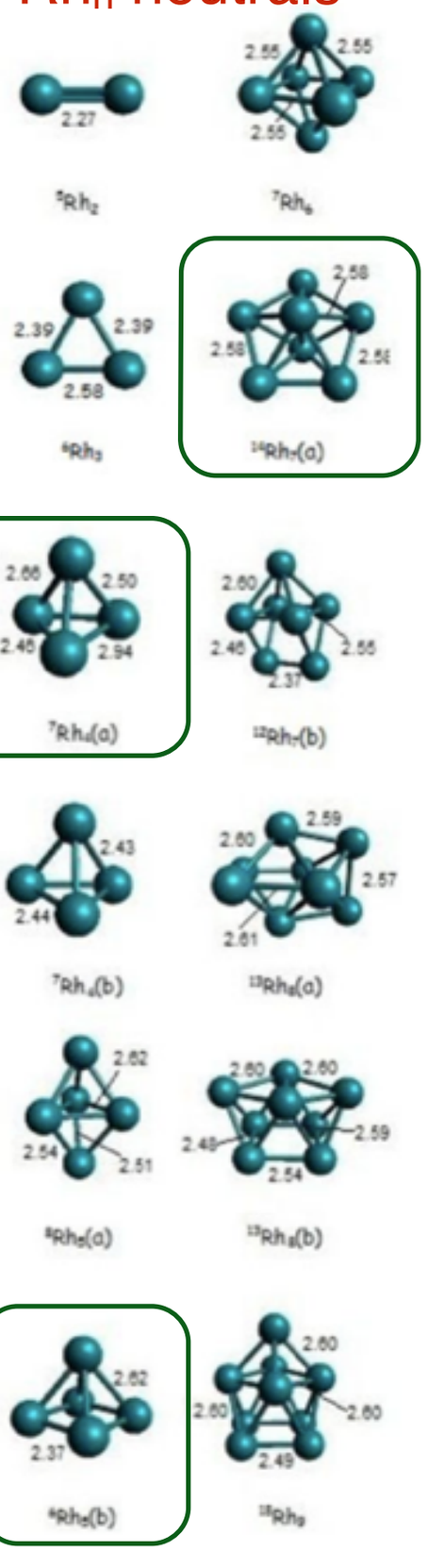


Rh_n anions



- At each size local minima for many structures (and spin states) identified for the anions
- Neutral energies at anion geometry calculated
- Local minima for the corresponding neutrals for possible spin states identified
- VDE and ADE calculated, compared with experiments

Rh_n neutrals

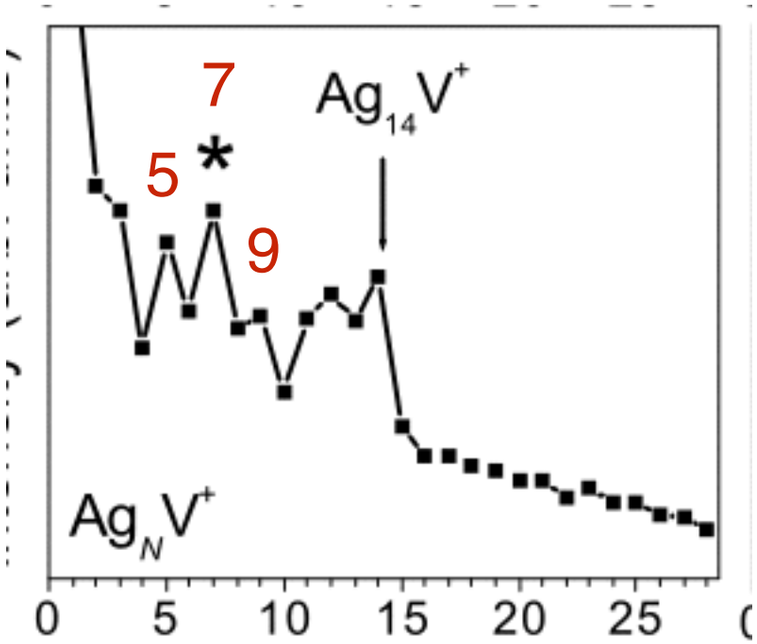


Cluster	Structure	Experimental		Calculated	
		ADE	VDE	ADE	VDE
Rh		–	1.10	–	1.20
Rh_2	Dimer	1.50	1.65	1.64	1.65
Rh_3	Isosceles triangle	1.0	1.2	1.16	1.27
Rh_4	Bent rhombus[a]	0.7	0.9	1.02	1.12
Rh_5	Triangular bi-pyramid[a]	1.4	1.47	1.32[a]	1.59[a]
Rh_5	Square pyramid[b]	1.4	1.47	1.40[b]	1.51[b]
Rh_6	Octahedron	1.4	1.5	1.44	1.46
Rh_7	Pentagonal bi-pyramid[a]	2.1	2.2	2.33[a]	2.74[a]
Rh_7	Capped-prism[b]	2.1	2.2	2.07[b]	2.10[b]

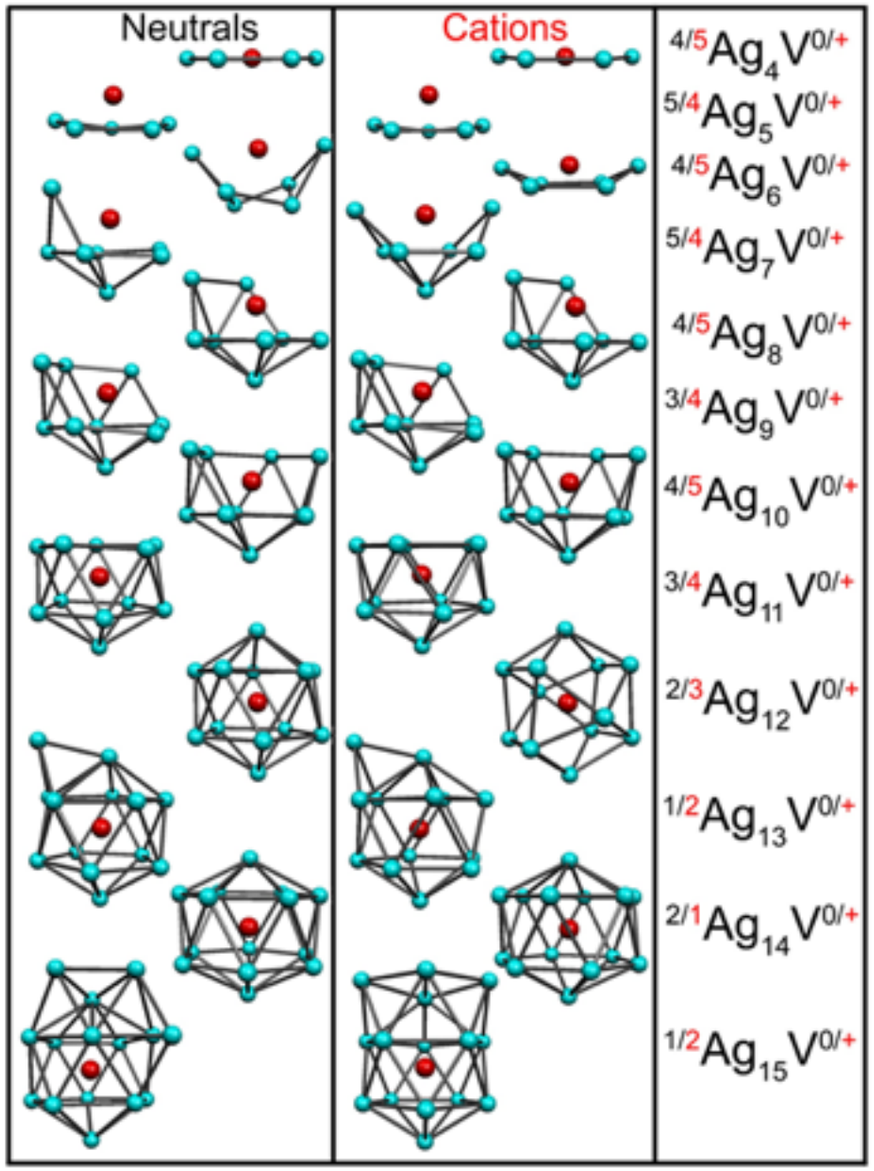
Beltran et al, EPJD 2013

Another example
TM-Ag clusters

Photofragmentation experiments

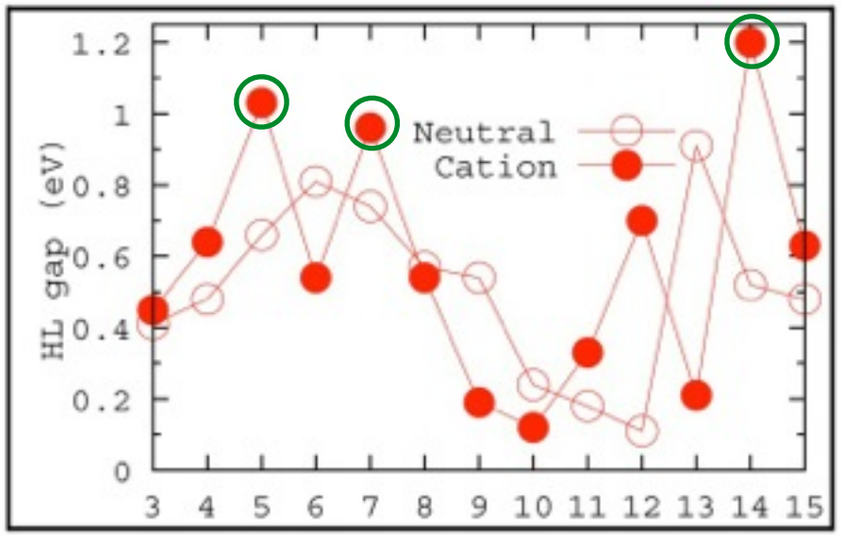


Janssens et al, PRL 2005

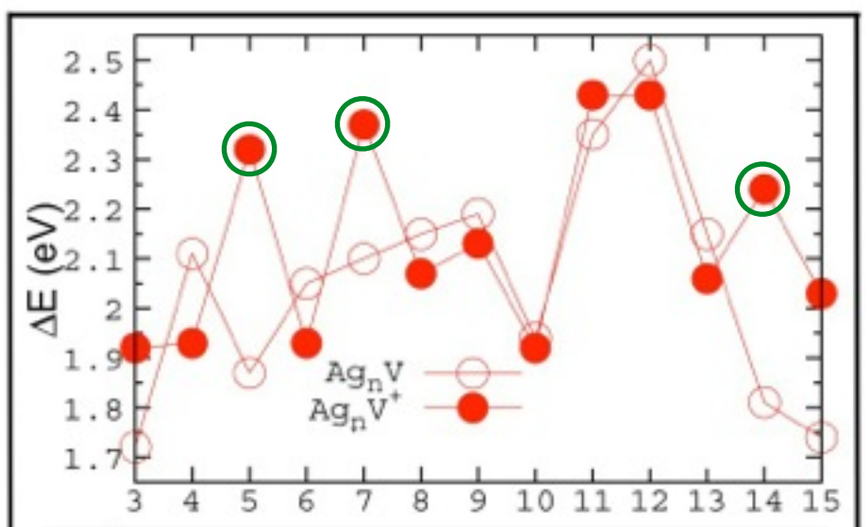


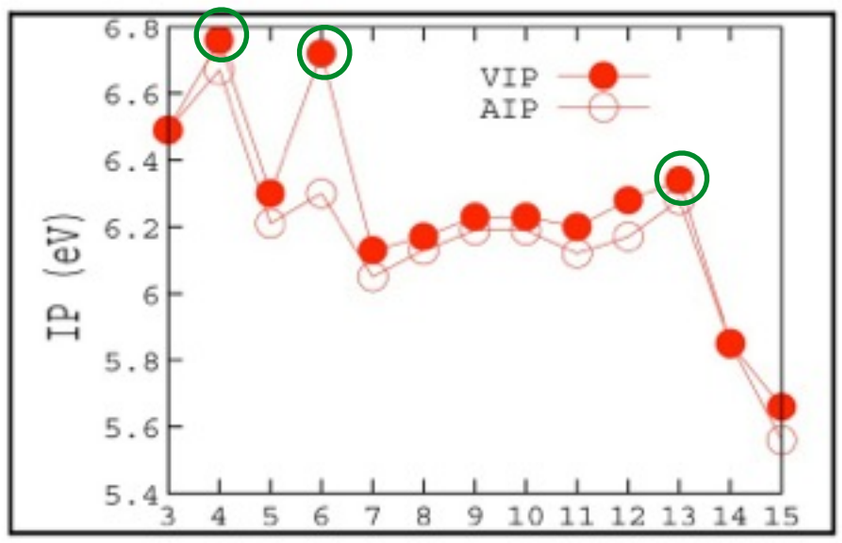
Medel et al, JACS 2014

Theoretical measures of stability



Medel et al, JACS 2014





These features not found if we
do not use the ground state structures
Structure once again

SCANNING TUNNELING MICROSCOPY OF Cu, Ag, Au AND Al ADATOMS, SMALL CLUSTERS, AND ISLANDS ON GRAPHITE

Eric GANZ *, Klaus SATTLER ** and John CLARKE

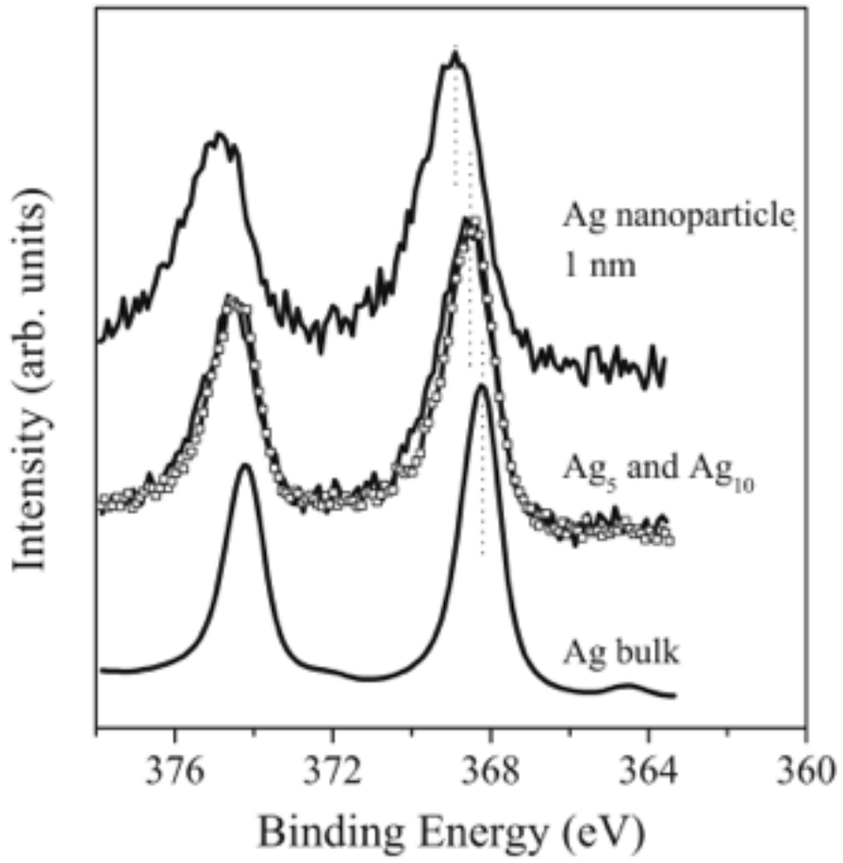
Department of Physics, University of California, Berkeley, CA 94720, USA
and
Center for Advanced Materials, Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

- Atoms deposited on graphite
- Isolated Ag adatoms always above ‘β’ site C atom
- Ag_2 dimers parallel to the surface

Contrast of Ag islands and mass selected clusters on graphite

Appl. Phys. A 90, 395 (2008)

- Ag atoms OR mass selected clusters soft landed on Ar sputtered graphite
  - Ag clusters 3-16 atoms mass selected and deposited
  - Ag atoms deposited to form islands
  - In the first case, Ag 3*d* core level shift is independent of cluster size
  - In the second case, Ag 3*d* core level shifts to higher BE's with decreasing island size
  - Core level shift in clusters is same as that in a 5 nm island
- Agglomeration of clusters ruled out in STM
- Difference in charge transfer from cluster/nano-particle to HOPG?
- Final state effects?

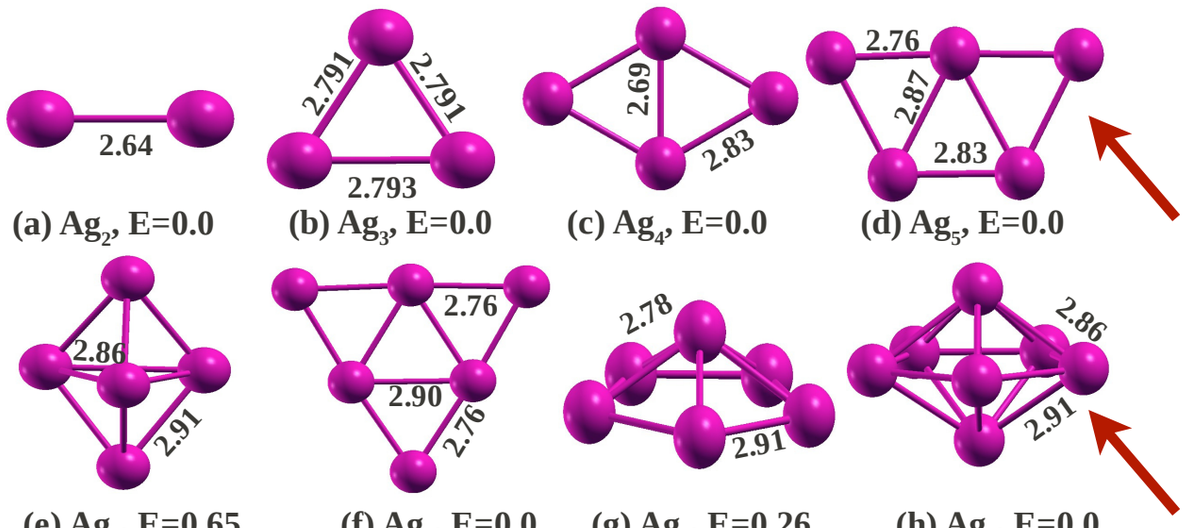


Clusters on stepped HOPG surfaces

EPJD 9, 523 (1999); EPJD 16, 297 (2001)

- Do not coalesce at 100 K, coalescence starts at ~155 K
- Deposited clusters very mobile on terraces at room temperature
- Get stuck along the steps
- Odd-even oscillations in the location of the Fermi level
- Clusters retain their structure and electronic identity

vdW-DF2 low energy isomers



(a) Ag_2, E=0.0 (b) Ag_3, E=0.0 (c) Ag_4, E=0.0 (d) Ag_5, E=0.0

(e) Ag_5, E=0.65 (f) Ag_6, E=0.0 (g) Ag_6, E=0.26 (h) Ag_7, E=0.0

(i) Ag_7, E=0.07 (j) Ag_7, E=0.11 (k) Ag_7, E=0.17 (l) Ag_7, E=0.19

(m) Ag_8, E=0.0 (n) Ag_8, E=0.005 (o) Ag_8, E=0.04 (p) Ag_8, E=0.06

(q) Ag_8, E=0.08 (r) Ag_8, E=0.09

L(S)DA structures optimized through evolutionary algorithm repotimized using vdW-DF2

Finding structures after deposition

- Clusters placed above different points on the graphite surface
- Many random random orientations generated by rotating them through random sets of Euler angles
- Relaxed without any constraints
- Spin polarized calculations

The methods

- Dispersion forces important in metal-graphite systems

- vdW-DF(2)

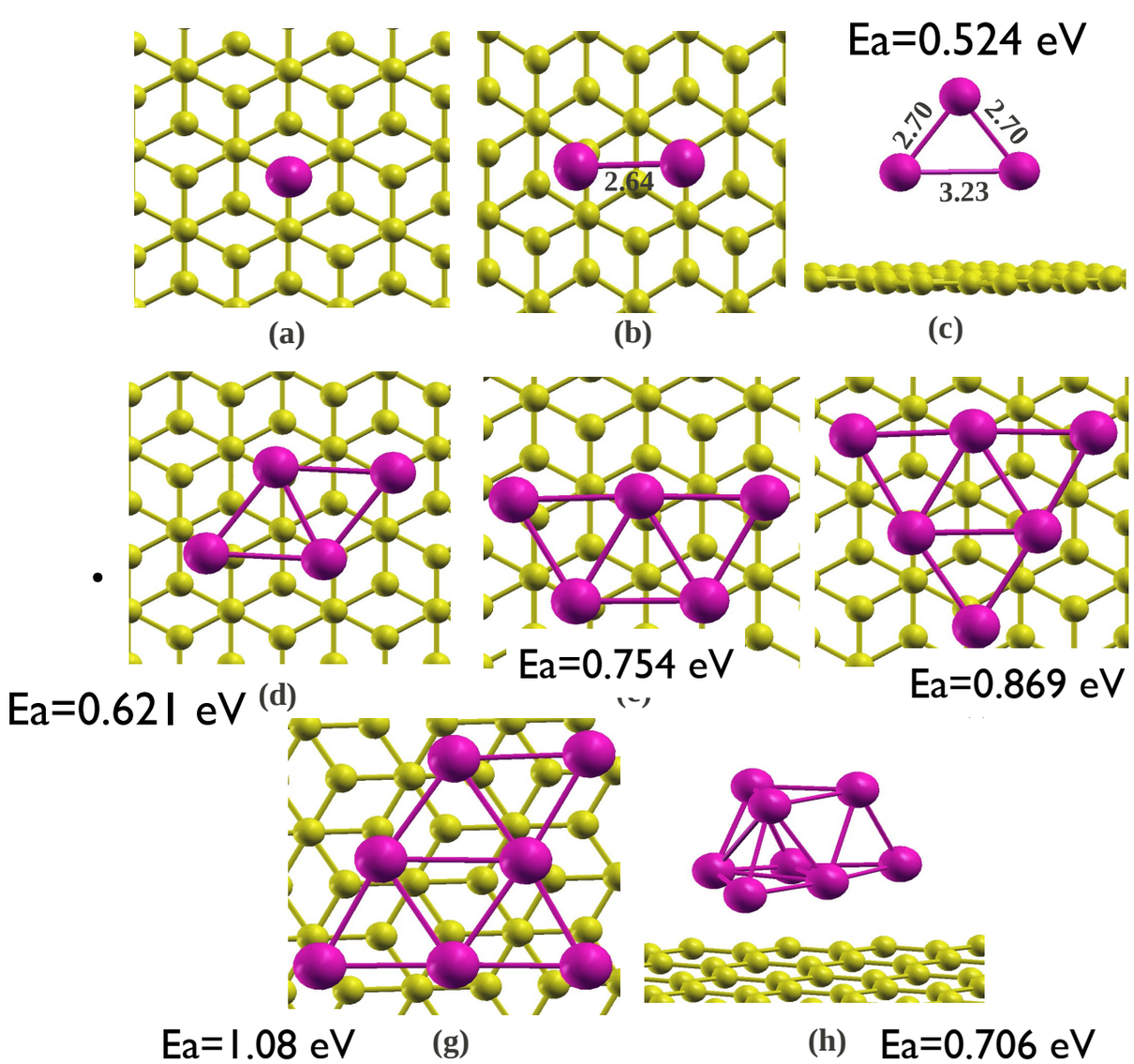
$$E_{xc} = E_x^{\mathrm{GGA}} + E_c^{\mathrm{LDA}} + E_c^{\mathrm{nl}}$$

$$E_c^{\mathrm{nl}} = \int dr_1 dr_2 \rho(\vec{r}_1)\phi(\vec{r}_1,\vec{r}_2)\rho(\vec{r}_2)$$

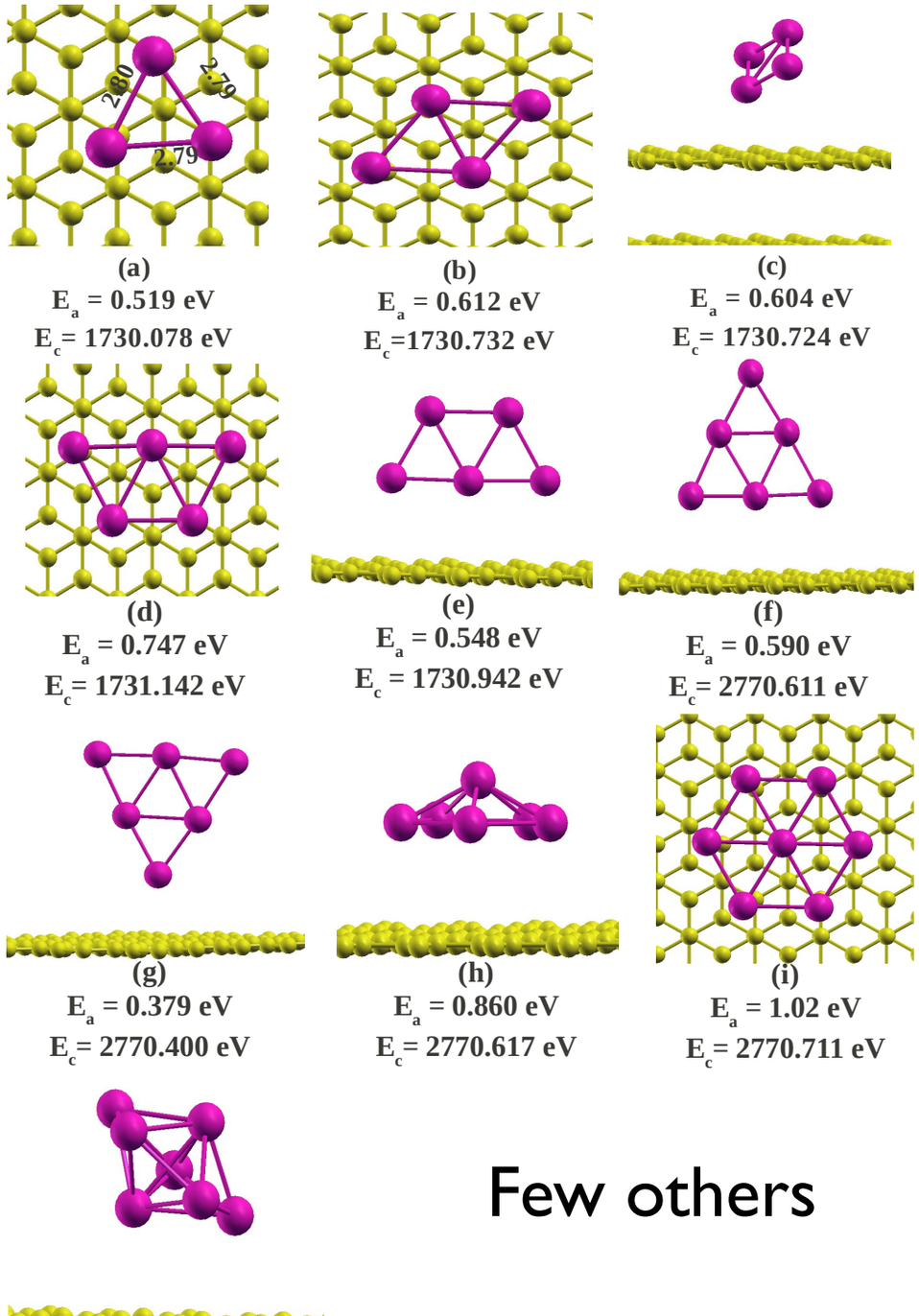
- GGA is revPBE in vdW-DF

- rPW86 in vdW-DF2

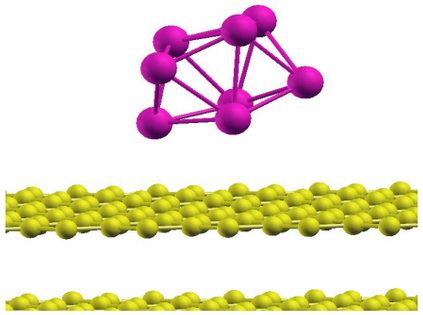
Some low energy deposited structures using vdW-DF2



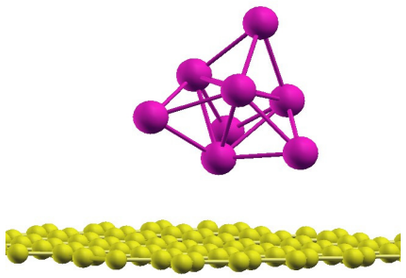
Highest E_a structures



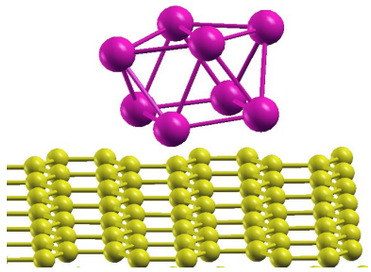
Few others



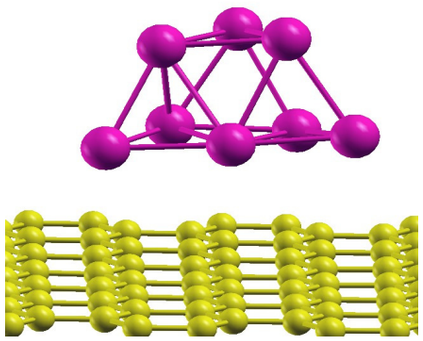
(a)
E_a = 0.57 eV
E_c = 3232.27 eV



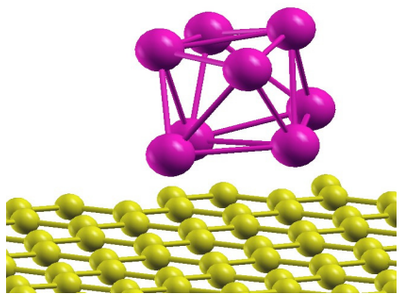
(b)
E_a = 0.61 eV
E_c = 3232.31 eV



(c)
E_a = 0.61 eV
E_c = 3232.27 eV



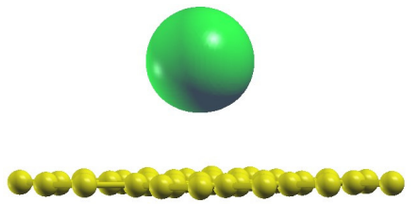
(d)
E_a = 0.70 eV
E_c = 3232.32 eV



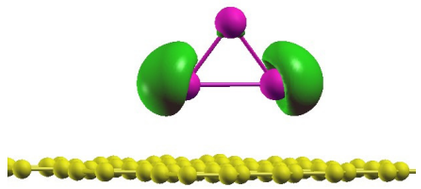
(e)
E_a = 0.64 eV
E_c = 3232.23 eV

- Some higher energy structures for Ag_8

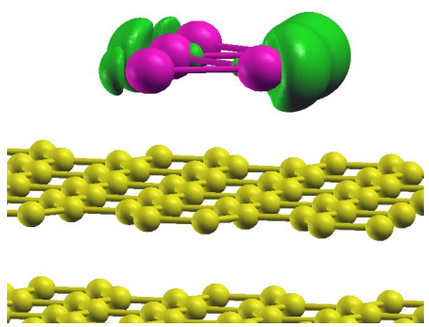
Spin density localized on the odd size clusters



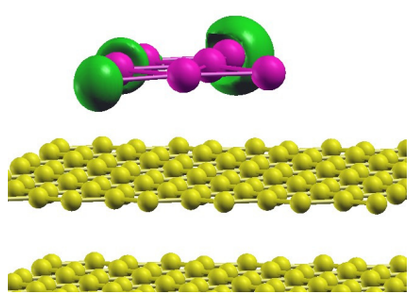
(a)



(b)



(c)



(d)

Details of silver clusters on graphite

Table 3: Details of silver clusters on graphite from vdW-DF2 studies. E_a and E_c are the adsorption energy and cohesive energy respectively; M is the magnetic moment and q is the charge transfer from the cluster to surface in terms of electronic charge. Z_r denotes the maximum relaxation of the C atoms on the top layer and ΔZ_c represents the maximum deviation of a top layer C atom from their average position.

Size	Figure reference	E_a (eV)	E_c (eV)	M (μ_B)	q (e)	Z_r (Å)	ΔZ_c (Å)
1	3(a)	0.215	922.17	0.99	0.01	-0.045	-0.006
2	3(b)	0.323	922.76	0.00	0.02	-0.082	-0.025
3	3(c)	0.524	1730.08	0.80	0.16	-0.064	-0.019
4	3(d)	0.621	1730.74	0.00	0.04	-0.094	-0.033
5	3(e)	0.754	1731.15	0.96	0.05	-0.099	-0.037
6	3(f)	0.869	2770.89	0.00	0.06	-0.099	-0.046
7	3(g)	1.086	2770.78	0.95	0.07	-0.071	-0.029
8	3(h)	0.706	3232.32	0.00	0.04	-0.067	-0.049

Singh and Sen, JCP 2013

Summary

- Finding the right structures for atomic clusters is absolutely important
  - Electronic structure and all other properties depend essentially on the structure
- GA-based global search works well
- For clusters containing ~10 atoms, `educated guess' is good enough in most cases we have studied
- No direct experimental information on structures at these sizes
- Only a synergy between theory and experiment can produce a knowledge about structures for small clusters

Thank you

Atoms deposited on stepped surface

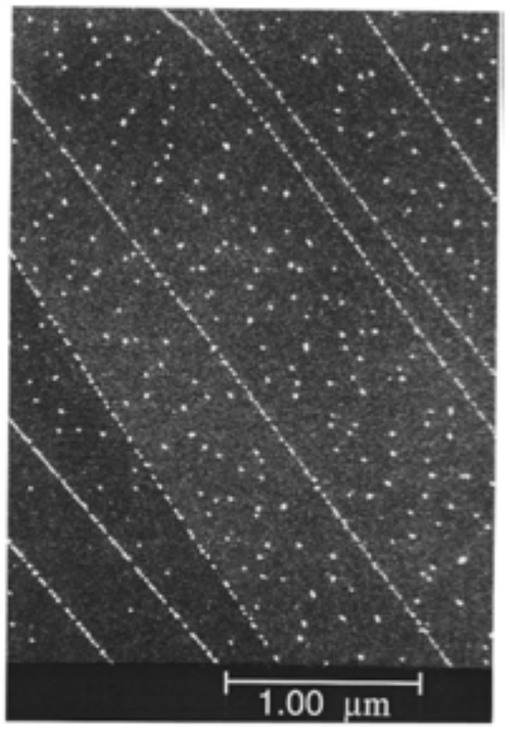


FIG. 1. A SEM image (2.89 μm×3.88 μm) showing Ag clusters on surface steps and terraces after deposition of Ag onto graphite (HOPG) for 2 s at a rate of 1.2×10^{13} cm^{-2} s^{-1} and temperature of 20 °C.

Low Temperature

FIG. 2. A SEM image (990 nm×1300 nm) of HOPG after Ag deposition for

High Temperature

High mobility on terraces

Trapped at step edges

Limited mobility along step edges

Ag adatom on graphite

- β site most stable as found in experiments, hollow site least favored
- Moment of the Ag atom is retained

Site	E_a(eV)	M (μ_B)
β	0.215	0.99
α	0.215	0.99
bridge	0.214	0.99
hollow	0.209	0.99

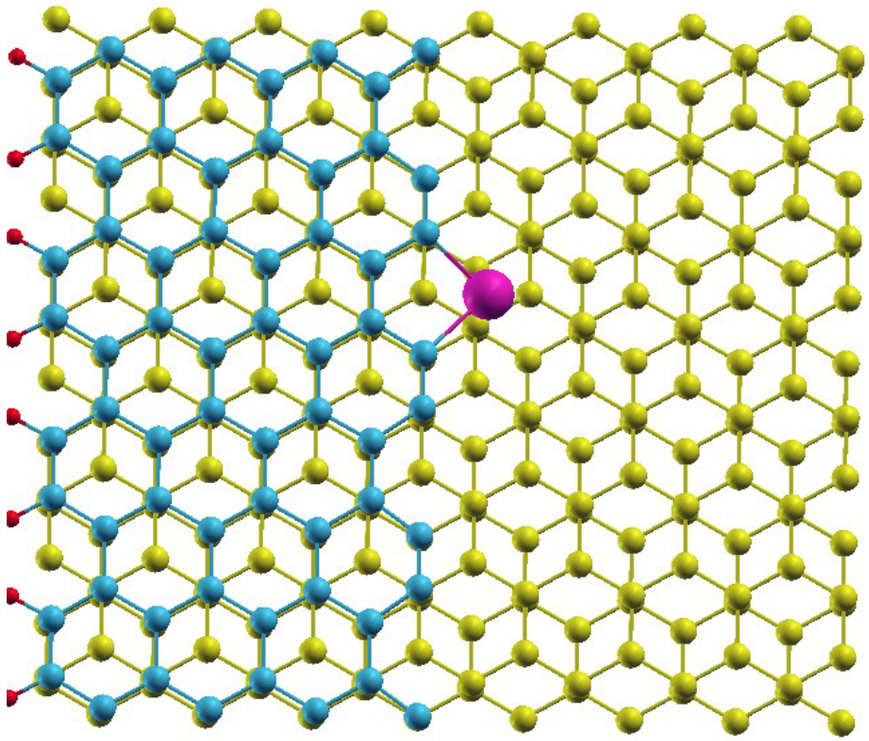
- Relative stability of larger clusters measured by two quantities
- Adsorption energy

$$E_a = E_T(\mathrm{Ag}_n) + E_T(\mathrm{graphite}) - E_T(\mathrm{Ag}_n/\mathrm{graphite}).$$

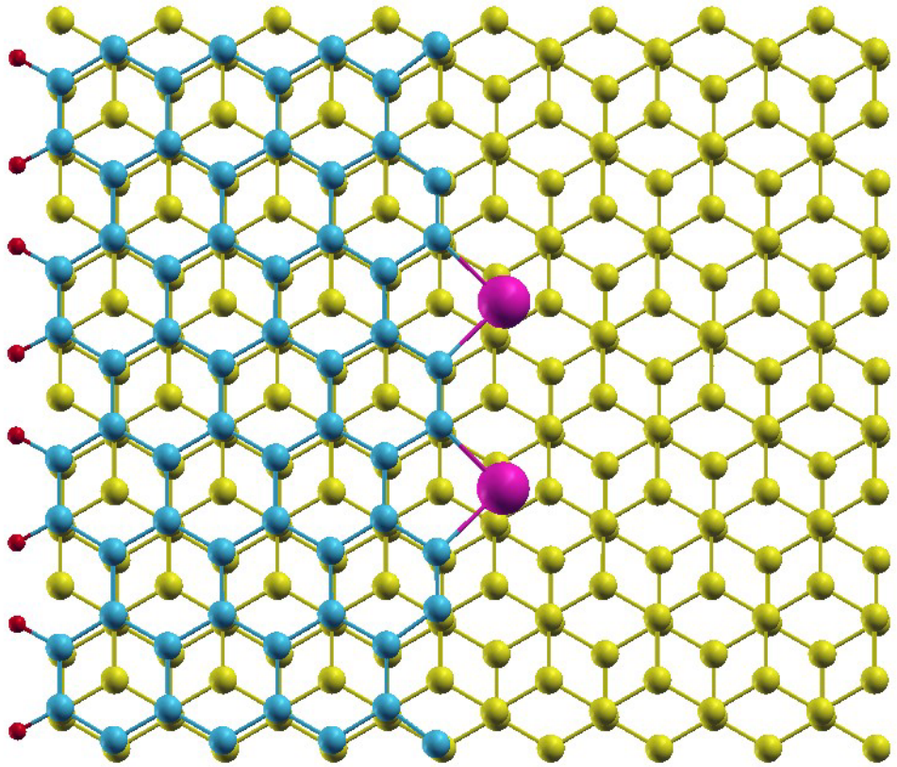
- Cohesive energy

$$E_c = nE_{\mathrm{Ag}} + N_{\mathrm{C}}E_{\mathrm{C}} - E_T(\mathrm{Ag}_n/\mathrm{graphite}).$$

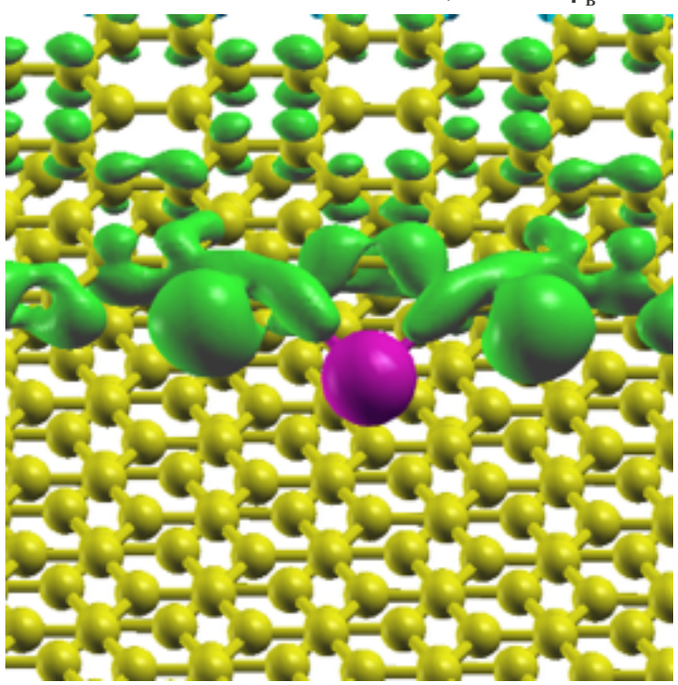
Adsorption of adatom and cluster on stepped surface



Ead = 3.36 eV, M = 0.98 μ_B



Ead = 4.74 eV, M = 0.0 μ_B



Adatoms bind at the arm-chair step

`Attracted' towards the step from the terraces

Large Ea compared to those on terraces

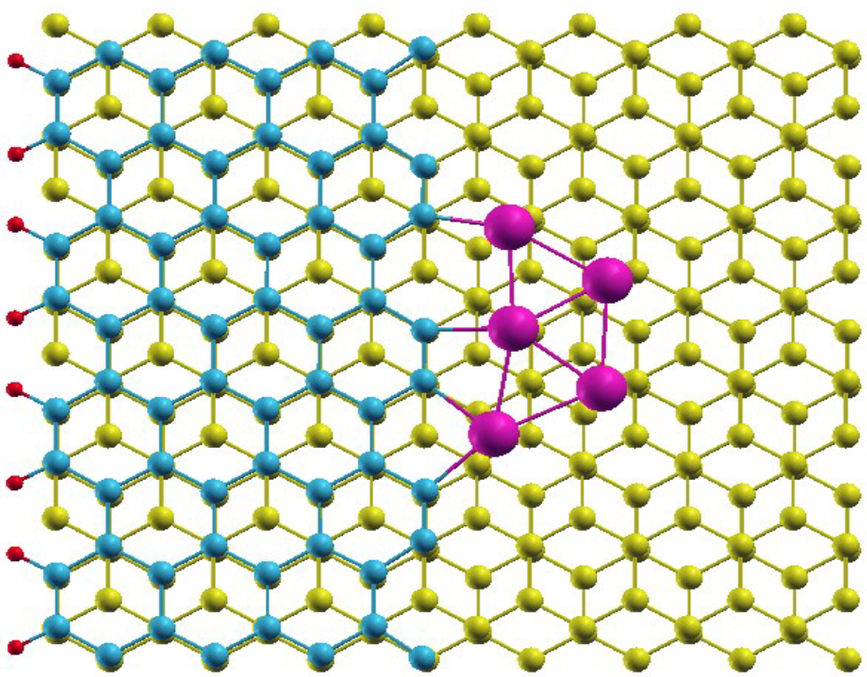
Dimer breaks

Larger clusters distorted significantly

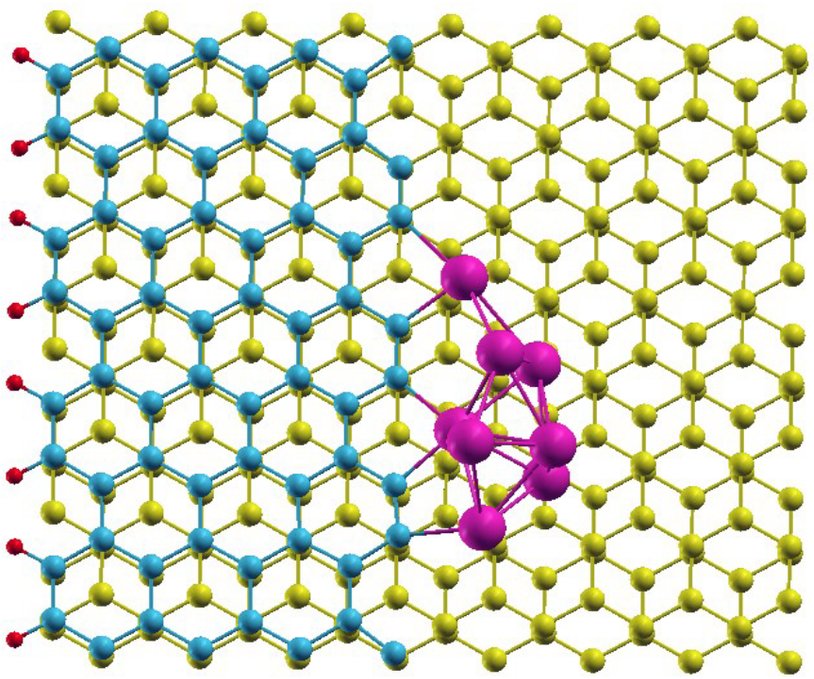
Substantial charge density along Ag-C bonds

... stepped surface ... finite T

- Lowest energy structures at T=0 for Ag_5 and Ag_8



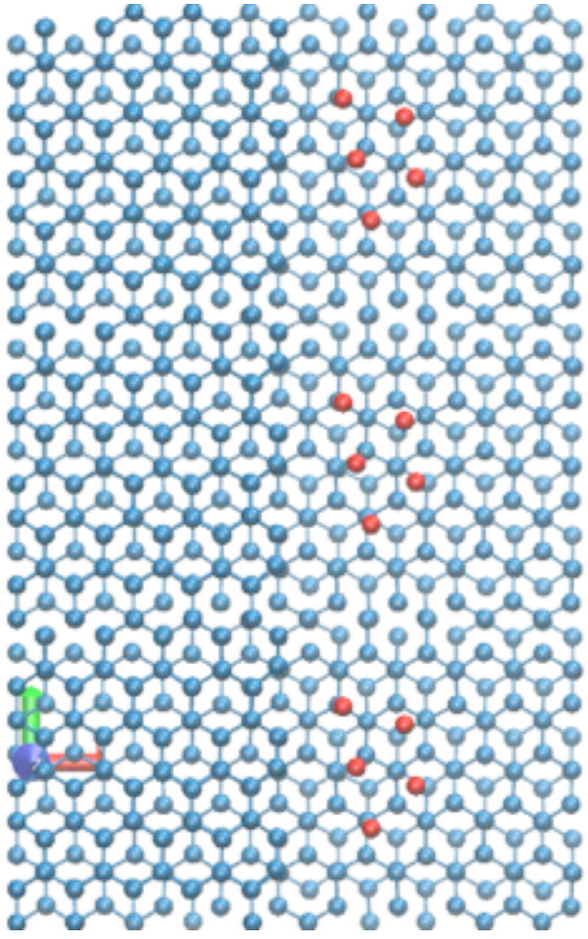
Ea = 6.06 eV, M = 0.99 μ_B



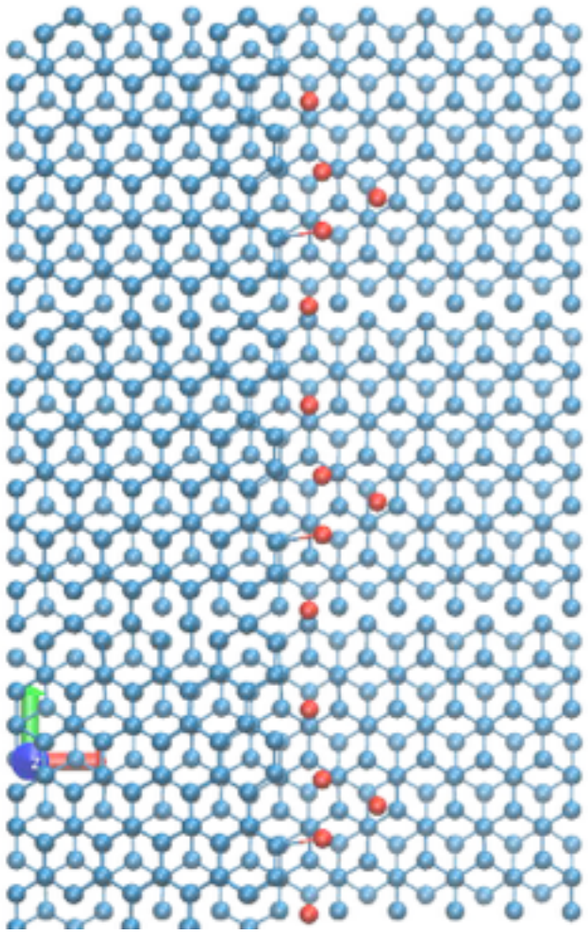
Ea = 5.54 eV, M = 0.0 μ_B

- Clusters break up to form linear chains along the step edges at finite T

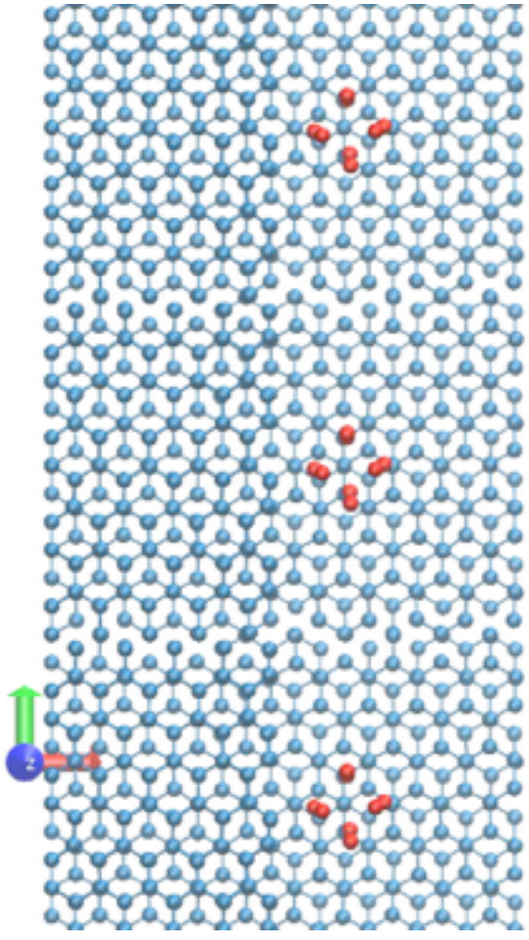
Dynamics at finite T



Ag_5 at T=600 K



Ag_5 at T=200 K



Ag_8 at T= 600 K

Direct search for global minimum
Global search

- Genetic algorithm (GA)
  - Identify the cost function that is be minimized (optimized in general)
  - Create a population, assign a `fitness' to each member
  - Select two members (**parents**) at a time for **crossover**
    - Members with higher fitness should have a greater probability of getting selected
    - Form **offsprings**, select them with certain probability
    - Repeat till you have the new generation of the same size
    - Repeat crossover on the new generation to propagate …
- Do occasional **mutation** moves