Geometries and stabilities of Ag-doped Si_n (n =1 - 13) clusters: a first-principles study

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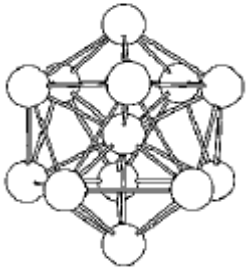
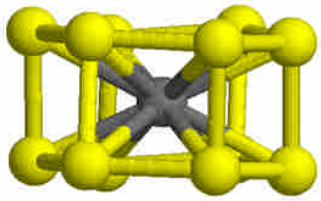
Chuang's Research Group

- Postdoctoral Researcher
  - Dr. Marvin Albao (Ph. D., Iowa State Univ. 2005)
    - Kinetic Monte Carlo simulations of surface systems
- Graduate Students
  - 謝昀頤 (碩二)
  - 許志強 (碩二)
  - 許嘉修 (碩二)
  - 黃治權 (碩一)
- Undergraduate Students
  - 邱議賢 (大四)

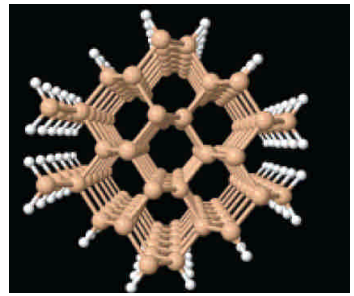
左至右：謝昀頤,許志強,吳傑龍,Marvin Albao,許嘉修, 莊豐權



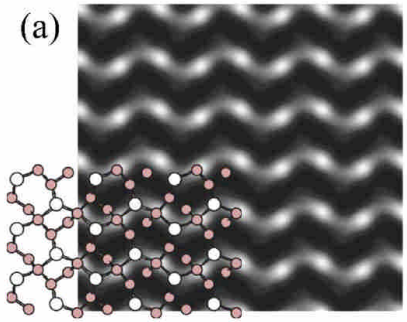
Research Interests



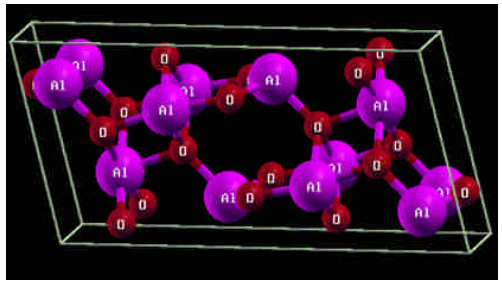
- (0-dim) Atomic clusters
- (1-dim) Nanowires and Nanotubes
  - Si nanowires



- (2-dim) Surface systems
  - High index surfaces
  - Metal-induced semiconductor reconstructions
  - Clusters on surfaces



- (3-dim) Crystals



Collaborators

- Dr. Kai-ming Ho, *Ames Lab and Iowa State U.*
- Dr. Cai-Zhuang Wang, *Ames Lab and Iowa State U.*
- Dr. Songyou Wang, *Fudan University, China (visiting)*
- Dr. Bei Liu, *Ames Lab (former graduate student)*
- Dr. T.-L. Chan, *U. of Tesax at Austin (former graduate student)*
- Dr. W. C. Lu, *Jilin University, China (visiting)*
- Mr. Ning Lu, *Ames Lab (graduate student)*

- Dr. C. V. Ciobanu, *Colorado School of Mines*
- Dr. C. Predescu, *U. of California, Berkeley*
- Dr. V. B. Shenoy, *Brown University*

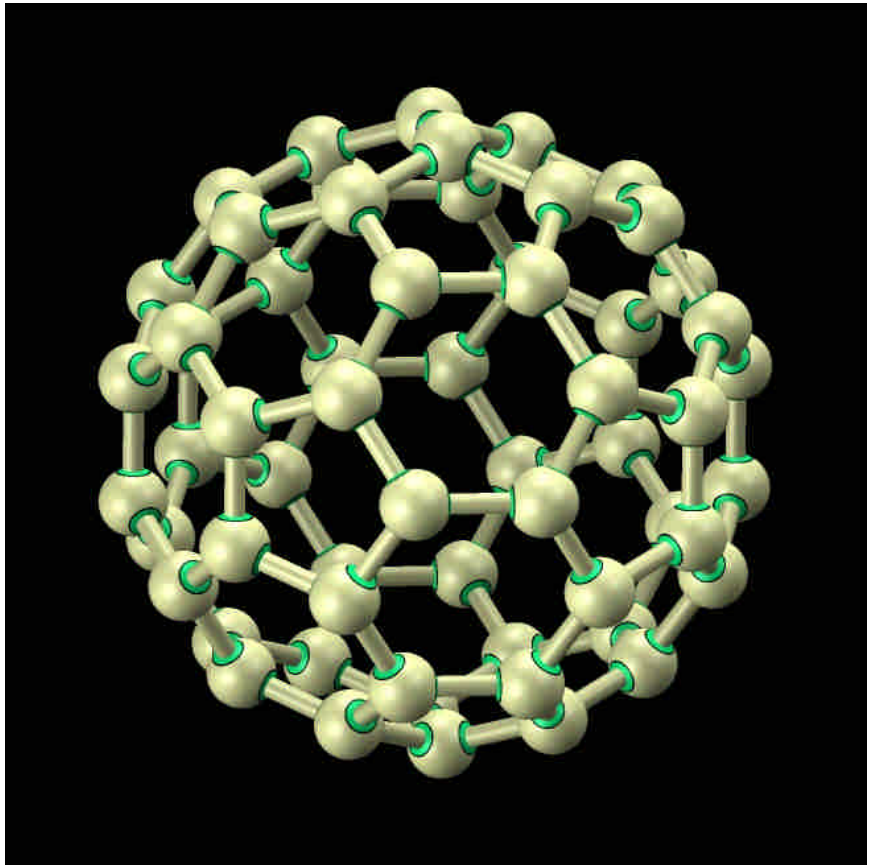
Outline of talk

- Geometries and stabilities of Ag-doped Si_n (n =1-13) clusters: a first-principles study
  - Introduction
  - Computational details
  - Result and Discussion
  - Conclusions

F.C. Chuang, Y.Y. Hsieh, C.C. Hsu and M.A. Albao, Geometries and stabilities of Ag-doped Si_n (n =1 - 13) clusters: a first-principles study, accepted in The Journal of Chemical Physics (2007).

Atomic clusters, Nano-cluster, Nano-particles

- Regarded as a phase of materials.
- Play an very important role in nanotechnology
- Structural studies of isolated clusters and of them on a surface



Atomic clusters

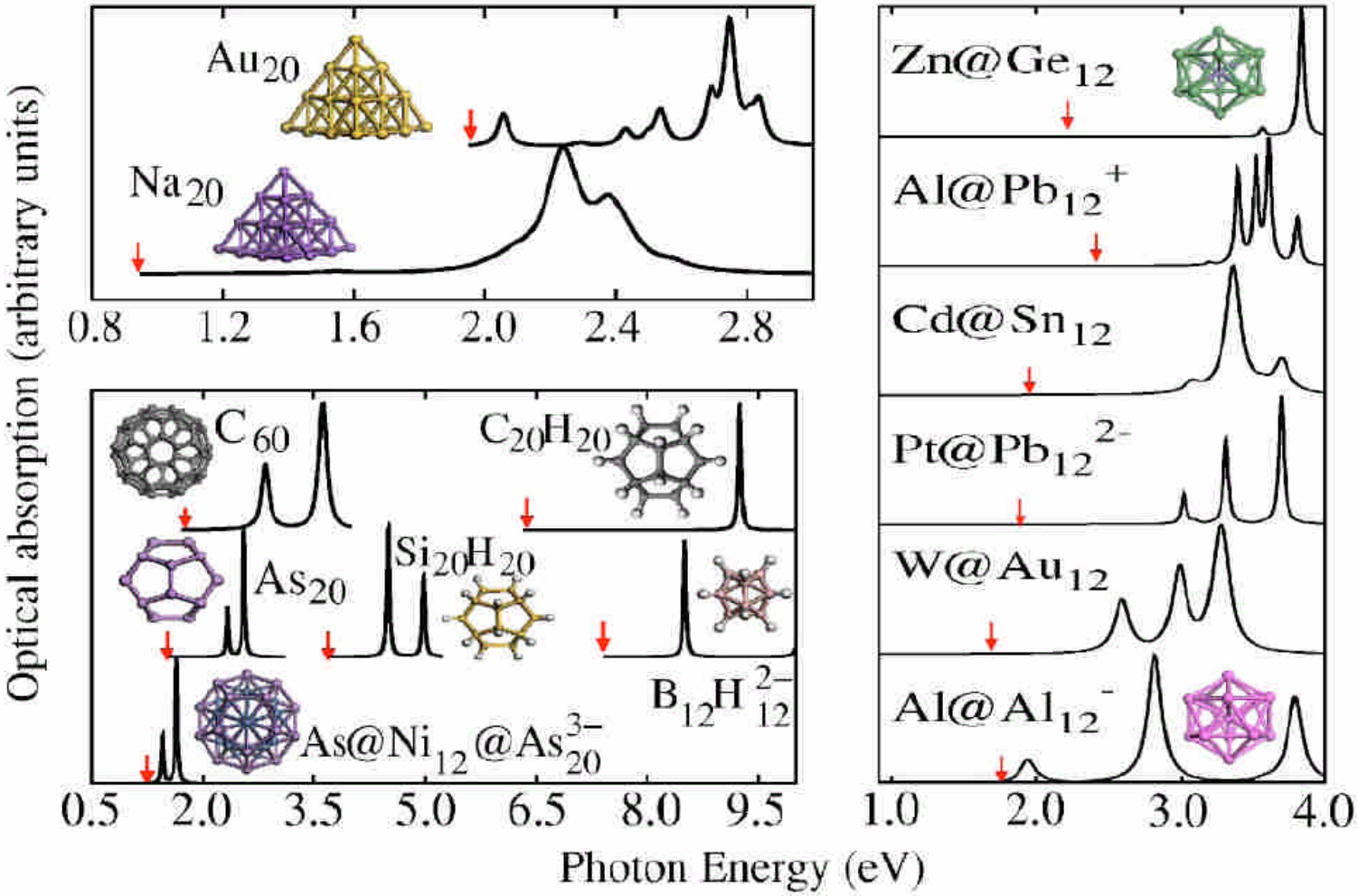
- **Fundamental Questions** need to be answered:
  - How do these structures nucleate and grow?
  - How do clusters transform from one structure to another as successive atoms are added during growth?
  - At what size does the bulk structure prevail?
  - atomic structure plays a critical role in determining all cluster properties
  - **theoretical and experimental determination of cluster structure are major obstacles**.
  - much structural information has been obtained *indirectly*, from experimental observations of other cluster properties
  - it has led to incomplete and sometimes ambiguous interpretation.

Recent developments

- *"A recent significant development innanostructures of silicon is the possibility to produce novel forms such as silicon fullerenes and nanotubes using metal encapsulation."*
- *"These are more stable than nanostructures formed from elemental silicon, have high symmetries and potential for mass production with size selection. Their **electrical, magnetic and optical properties** can be changed by changing the metal atoms."*

Abhishek Kumar Singh, Vijay Kumar and Yoshiyuki Kawazoe, *Metal encapsulated nanotubes of silicon and germanium*, Journal of Materials Chem., 14 555 (2004).

Tunable optical properties



Calculated absorption spectra for 14 icosahedral, dodecahedral, and tetrahedral clusters. All spectra were broadened by 0.06 eV to simulate finite temperature. The arrow indicates the first singlet excitation.

Rui-Hua Xie, Garnett W. Bryant, Jijun Zhao, Tapas Kar, and Vedene H. Smith, Jr.
Tunable optical properties of icosahedral, dodecahedral, and tetrahedral clusters
Phys. Rev. B 71, 125422 (2005)

Controlling HOMO-LUMO gap =>optical

Formation of Metal-Encapsulating Si Cage Clusters

- They expect *a metal-encapsulating Si cluster* to act as a tunable building block of new phases of materials.
- For instance, it will have a *HOMO-LUMO gap* that can be controlled by choosing the endohedral metal atom.

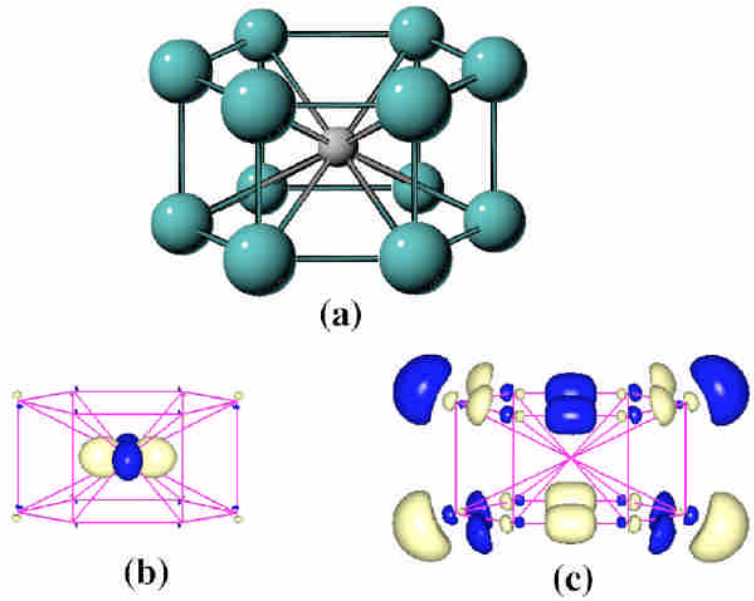
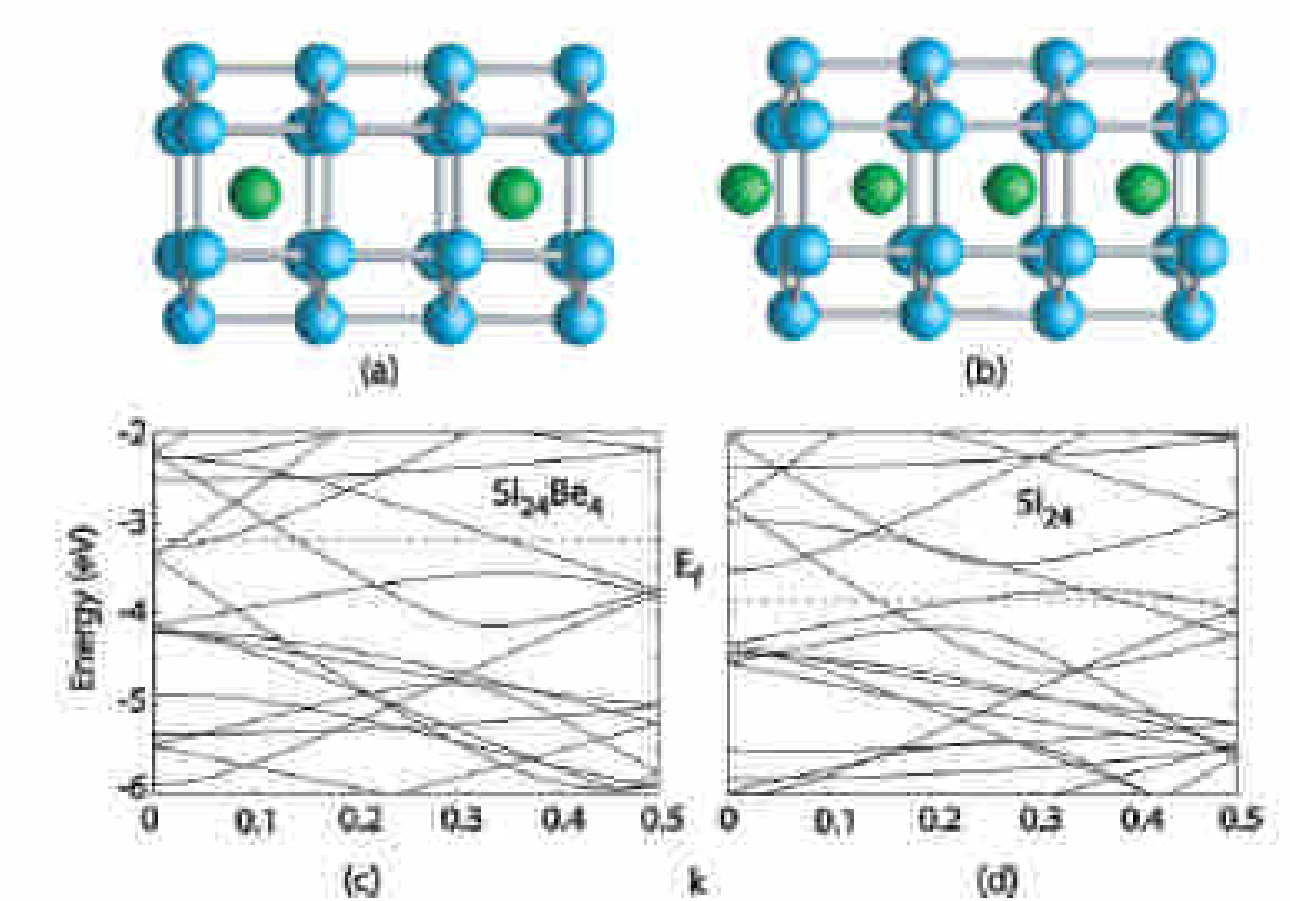


FIG. 1. (Color online) (a) The hexagonal prism cage structure of 12 Si atoms with D_{6h} symmetry with a TM atom at the center. (b) The singly occupied state in the majority spin channel for $V@Si_{12}$ localized on the TM atom. (c) The LUMO level for the same cluster.

H Hiura, T Miyazaki, and T. Kanayama, *Formation of Metal-Encapsulating Si Cage Clusters* , PRL 86, 1733, (2001)
P. Sen and L. Mitas, *Electronic structure and ground states of transition metals encapsulated in a Si12 hexagonal prism cage*, Phys. Rev. B 68, 155404 (2003)

Metal encapsulated nanotubes of silicon and germanium



Abhishek Kumar Singh, Vijay Kumar and Yoshiyuki Kawazoe, *Metal encapsulated nanotubes of silicon and germanium*, Journal of Materials Chem., 14 555 (2004).

Magnetic moments of metal-caged Si clusters

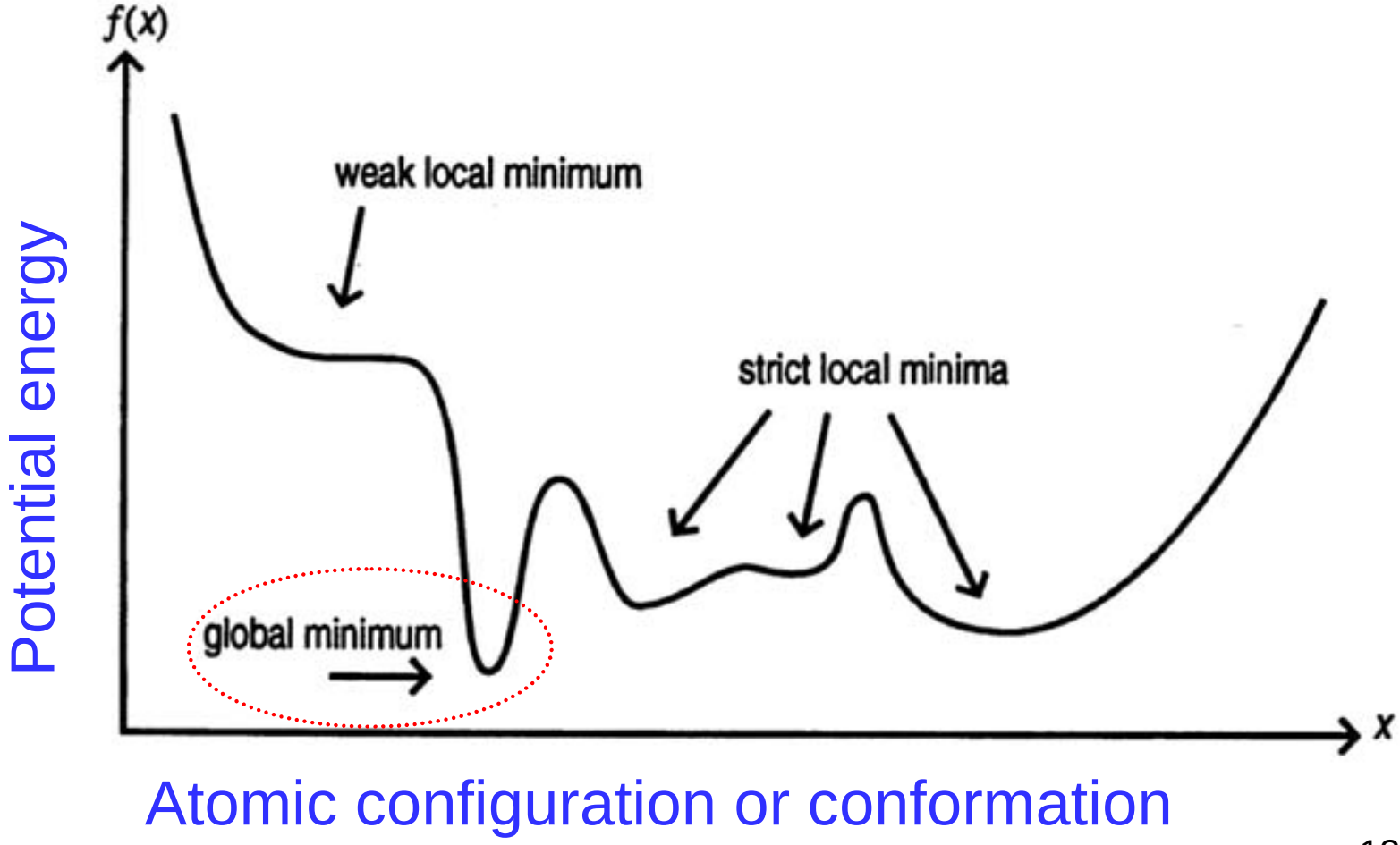
- computationally prediction: metal-encapsulated icosahedral superatoms of germanium and tin, $ZnGe_{12}$ and $CdSn_{12}$, with large HOMO–LUMO gaps or $MnGe_{12}$ and $MnSn_{12}$, with high (5 μB) magnetic moments.

- Magnetic moment => nano-spintronics applications

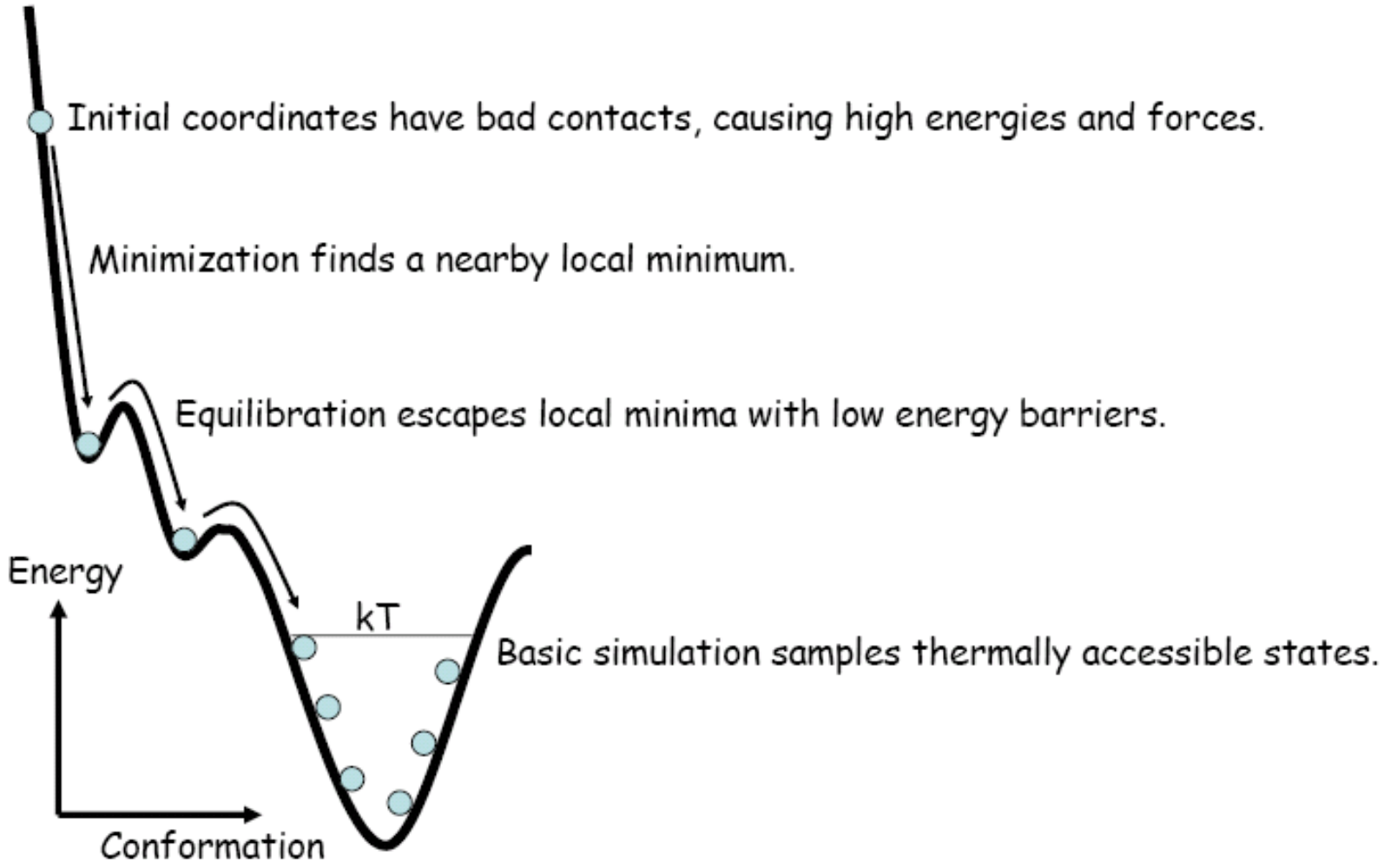
Potential Energy Surface

No matter what level of material design you use, potential energy is expressed as a function of atomic configuration.

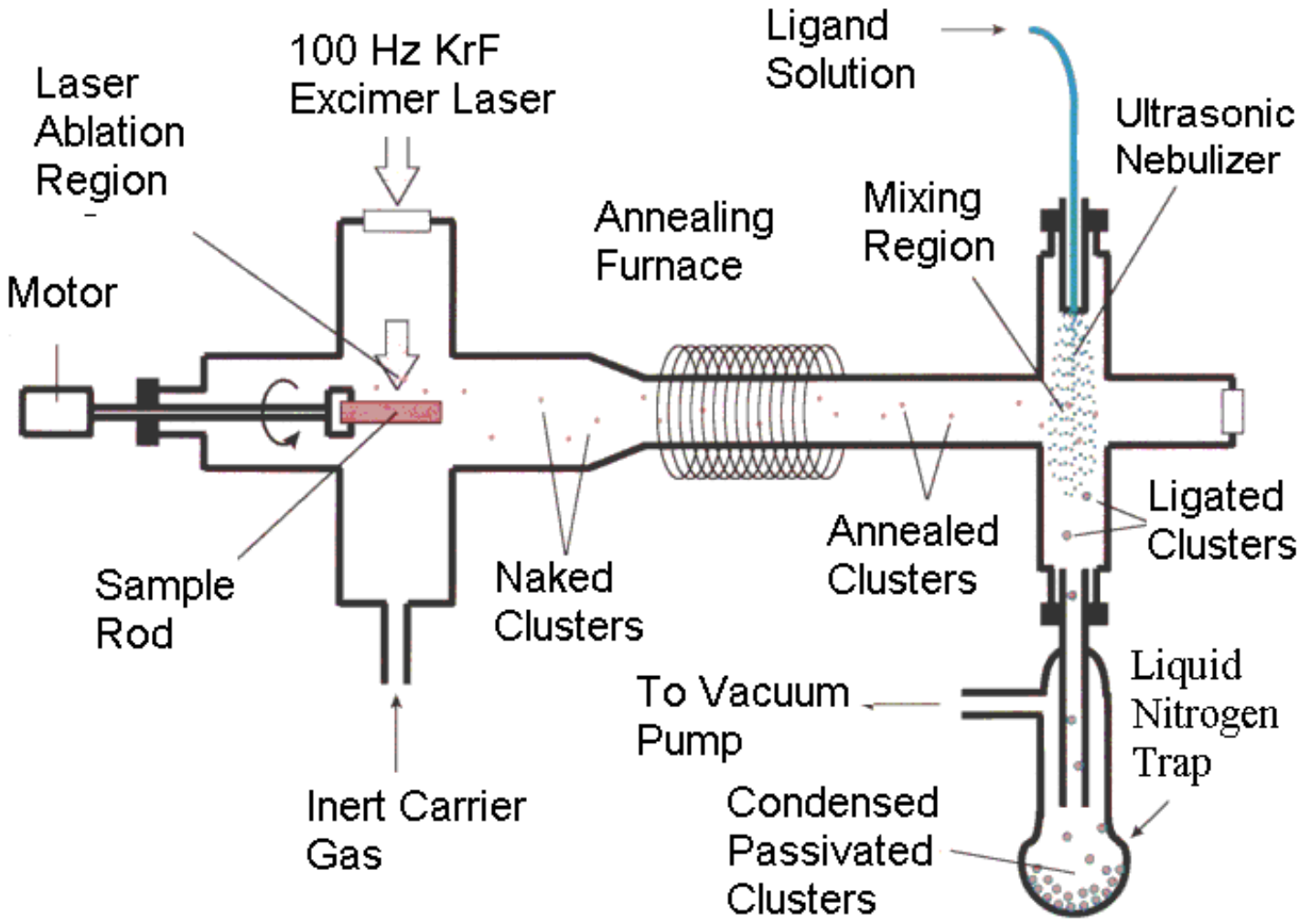
Question: how to obtain the global minimum structure.



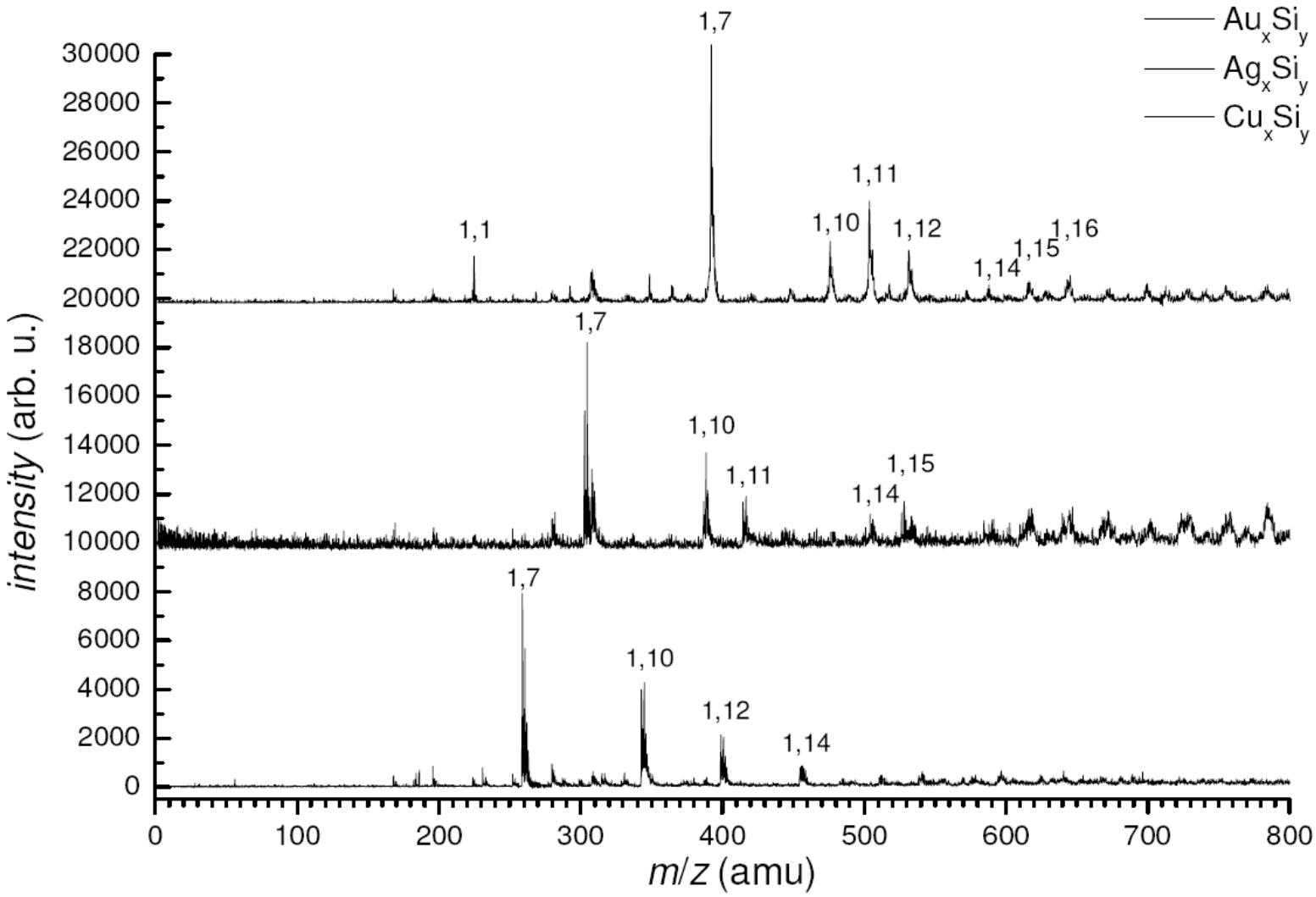
Simulating annealing MD approach to obtain the local minima



Experimental finding



Mass Spectra for Metal-Silcon clusters



The mass spectra obtained for metal-silicon clusters.

J. B. Jaeger, T. D. Jaeger, and M. A. Duncan, *Photodissociation of Metal-Silicon Clusters: Encapsulated versus Surface-Bound Metal*, J. Phys. Chem. A, Vol. 110, No. 30, 2006

Photo-dissociation of mass selected $AgSi_7^+$ and $AgSi_{10}^+$

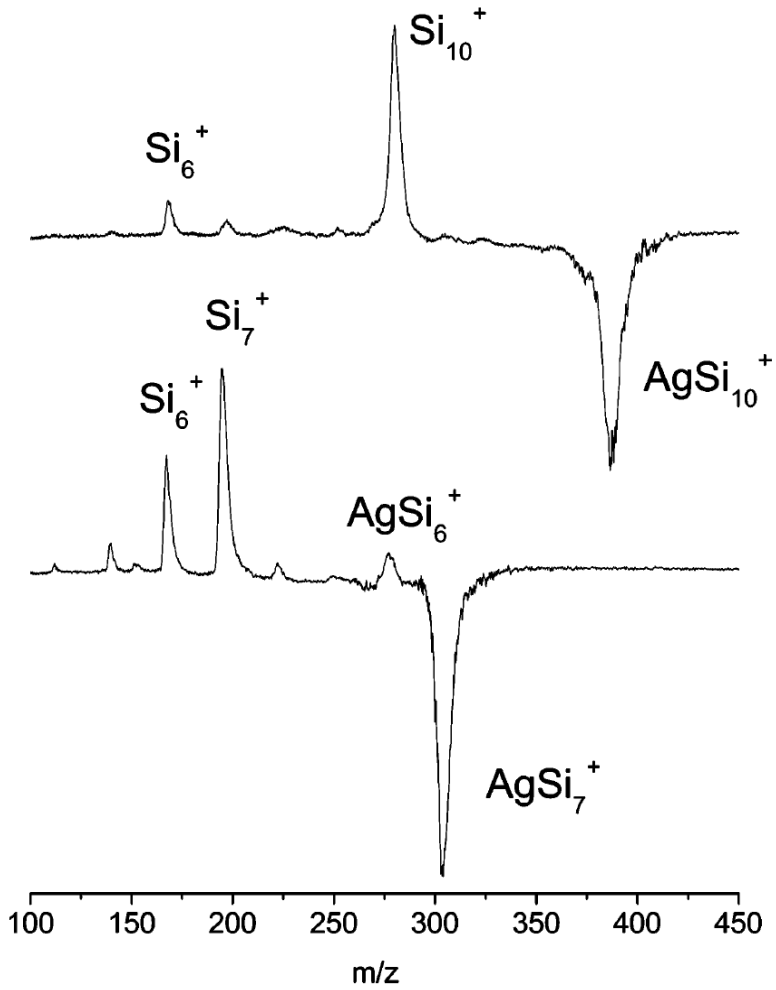


Figure 2. Photodissociation of mass-selected $AgSi_7^+$ and $AgSi_{10}^+$ at 532 nm.

J. B. Jaeger, T. D. Jaeger, and M. A. Duncan, *Photodissociation of Metal-Silicon Clusters: Encapsulated versus Surface-Bound Metal*, J. Phys. Chem. A, Vol. 110, No. 30, 2006

July. 10, 2007

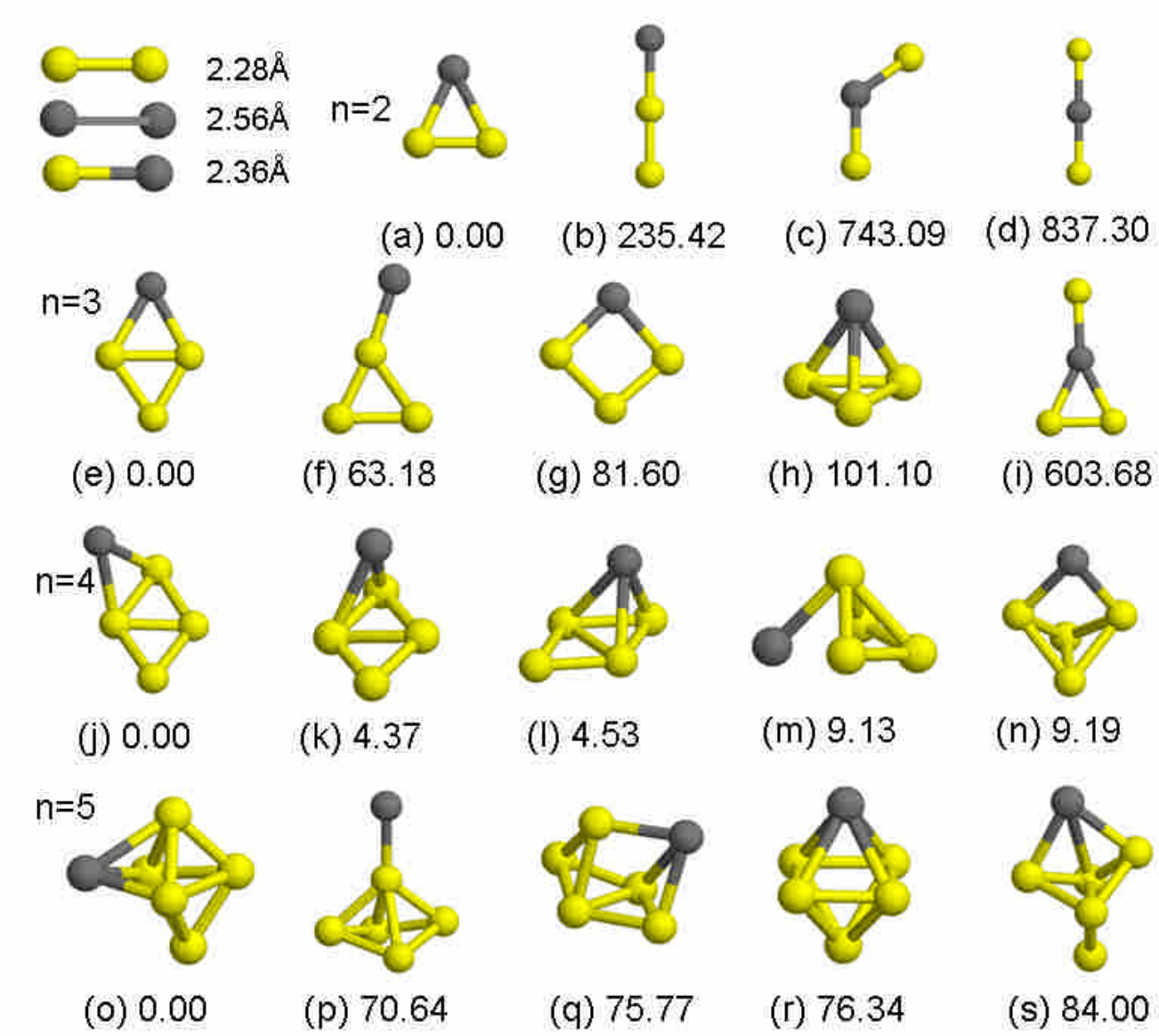
Question needs to be answered

- Whether Ag-doped Si clusters is a good candidates for future applications?
- A systematical study is highly desired to answer this question.

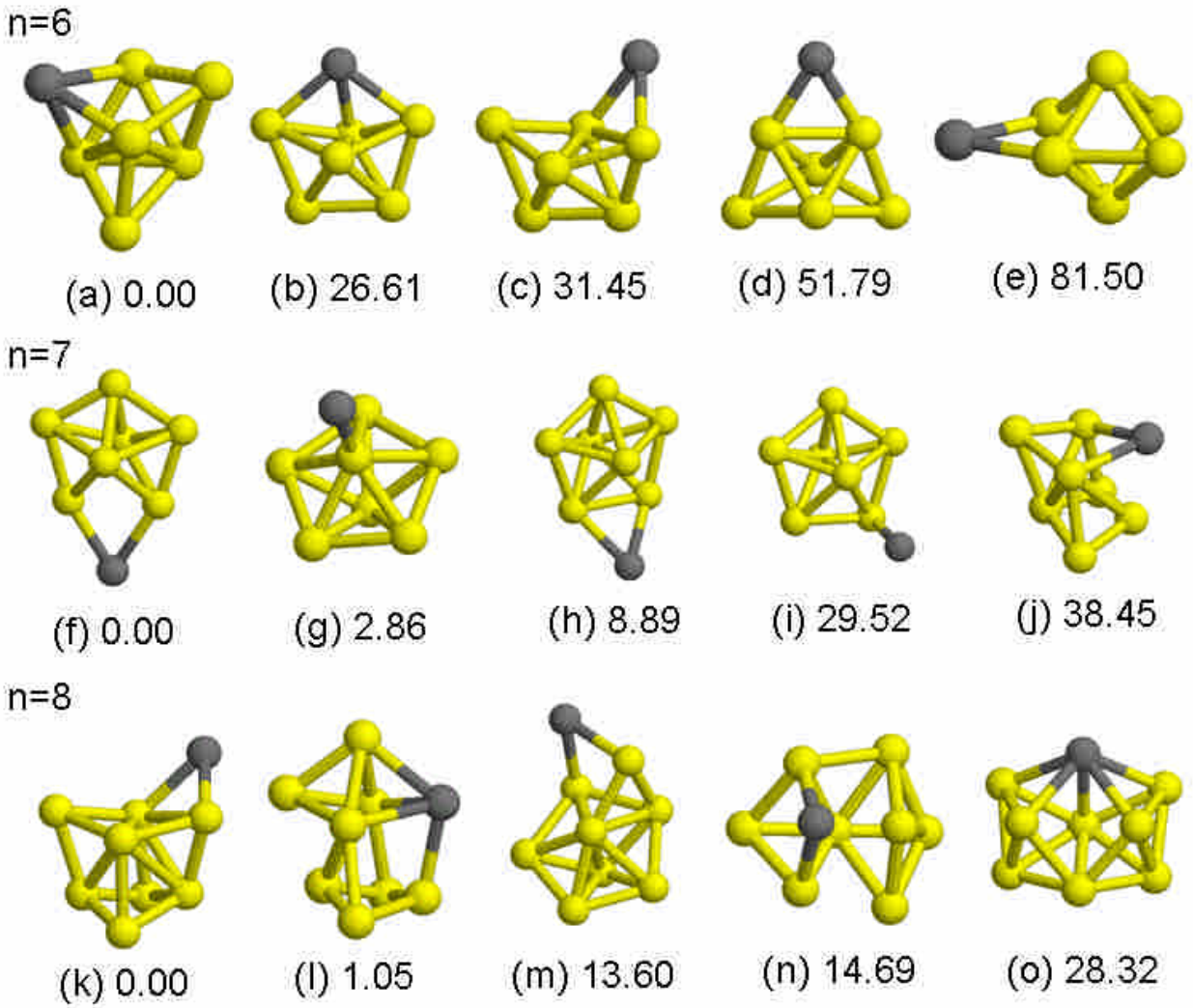
Computational Methods

- Ag has a filled $4d^{10}$ shell combined with a $5s^1$ valence shell.
- **Electron Configuration:** $[Kr]5s^14d^{10}$
- generalized gradient approximation (GGA) to spin polarized density functional theory using projector-augmented-wave potentials (PAW), as implemented in VASP.
- The kinetic energy cutoff is set to 249.8 eV (18.36 Ry).
- The structural optimization is done with the conjugate gradient (CG) algorithm and without symmetry until the forces on the atoms are less than 0.001 eV/Ang.
- For the AgSi_{n} and Si_{n} clusters, the length of the supercell is set to 15 Ang.
- In order to optimize certain proposed models, a quasi-Newtonian algorithm was used to relax models to their local minima.

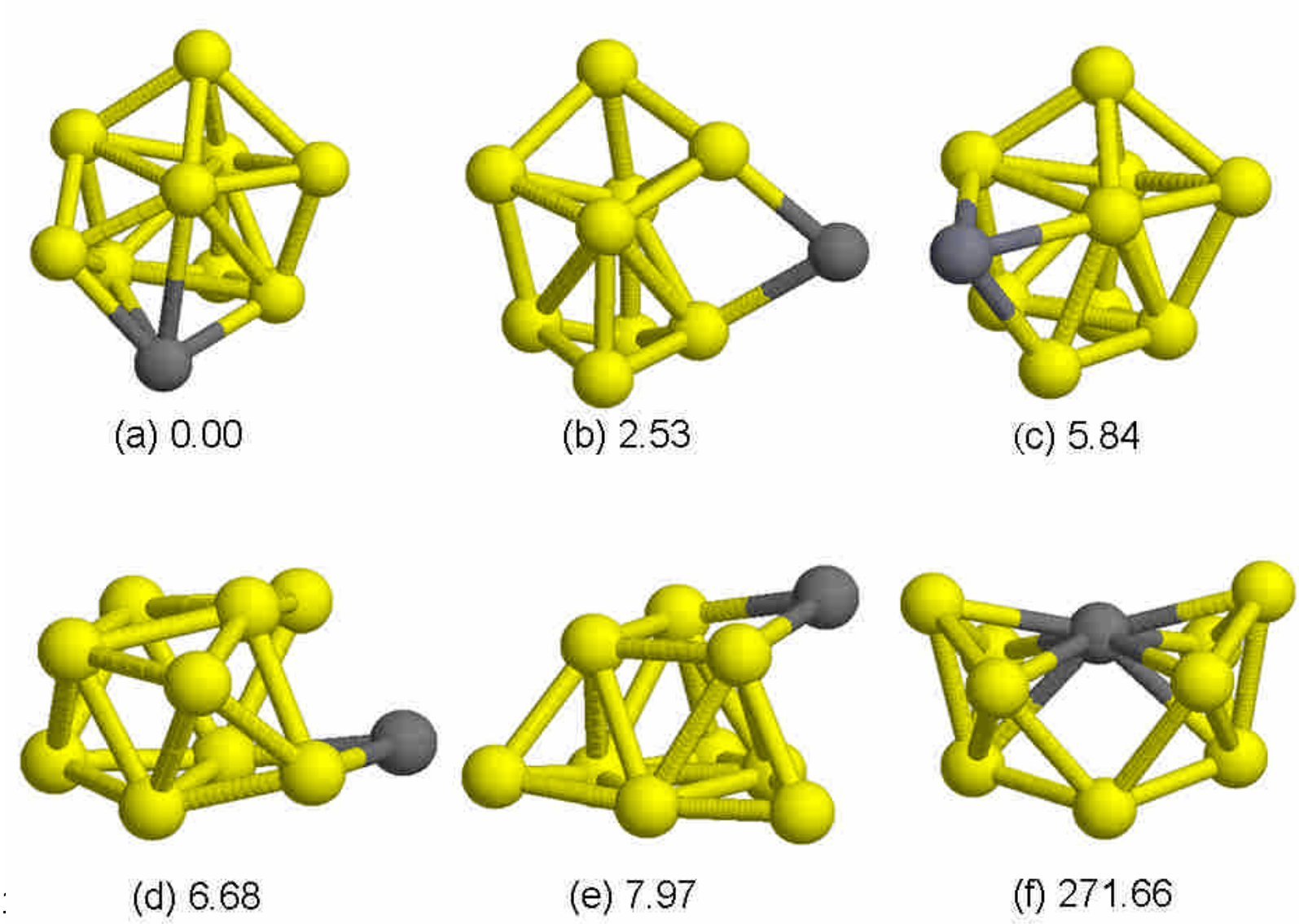
$AgSi_n$ (n=1 – 5)


2.28Å
2.56Å
2.36Å
n=2
(a) 0.00
(b) 235.42
(c) 743.09
(d) 837.30
n=3
(e) 0.00
(f) 63.18
(g) 81.60
(h) 101.10
(i) 603.68
n=4
(j) 0.00
(k) 4.37
(l) 4.53
(m) 9.13
(n) 9.19
n=5
(o) 0.00
(p) 70.64
(q) 75.77
(r) 76.34
(s) 84.00

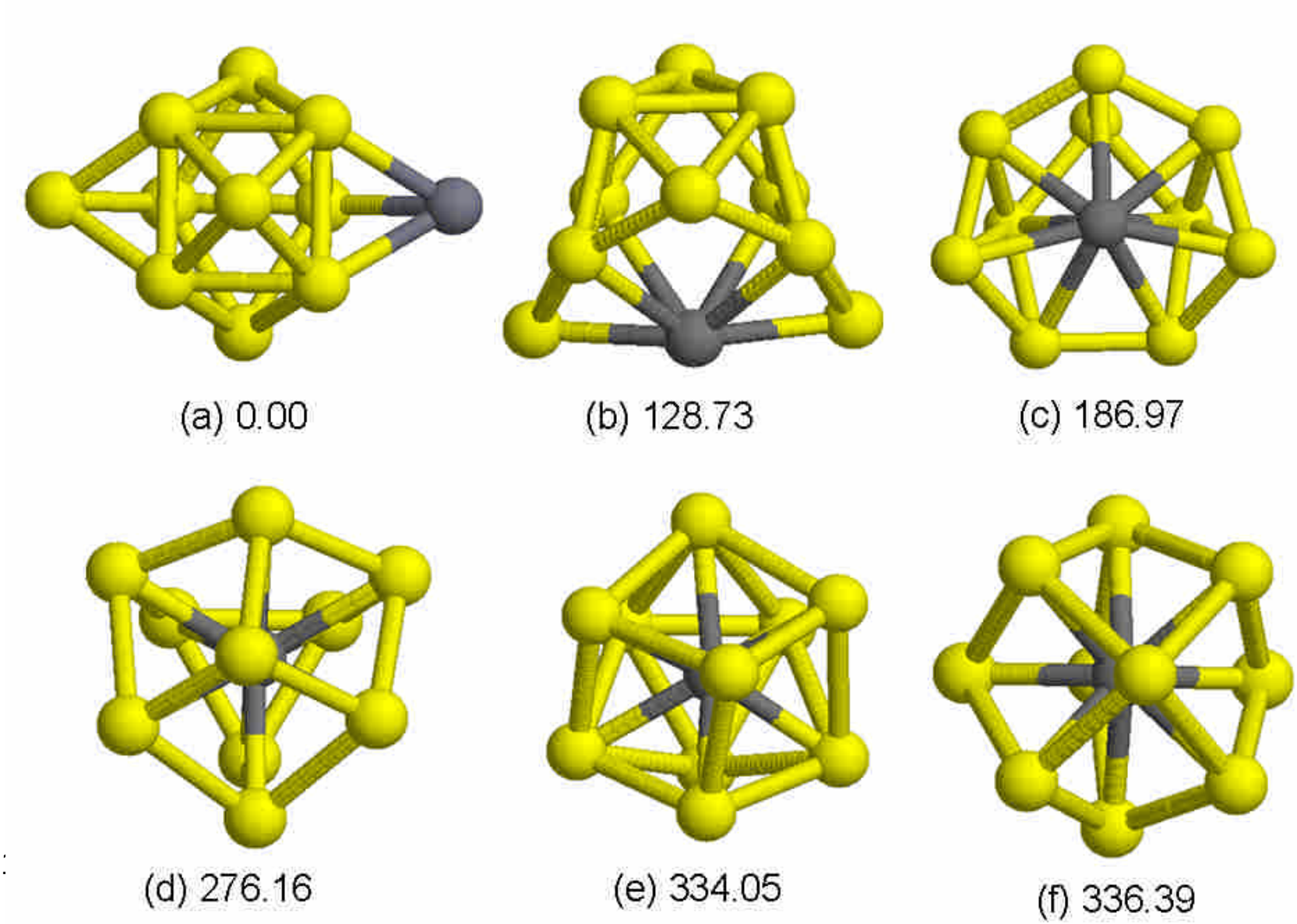
$AgSi_n$ (n=6 – 8)


n=6
(a) 0.00
(b) 26.61
(c) 31.45
(d) 51.79
(e) 81.50
n=7
(f) 0.00
(g) 2.86
(h) 8.89
(i) 29.52
(j) 38.45
n=8
(k) 0.00
(l) 1.05
(m) 13.60
(n) 14.69
(o) 28.32

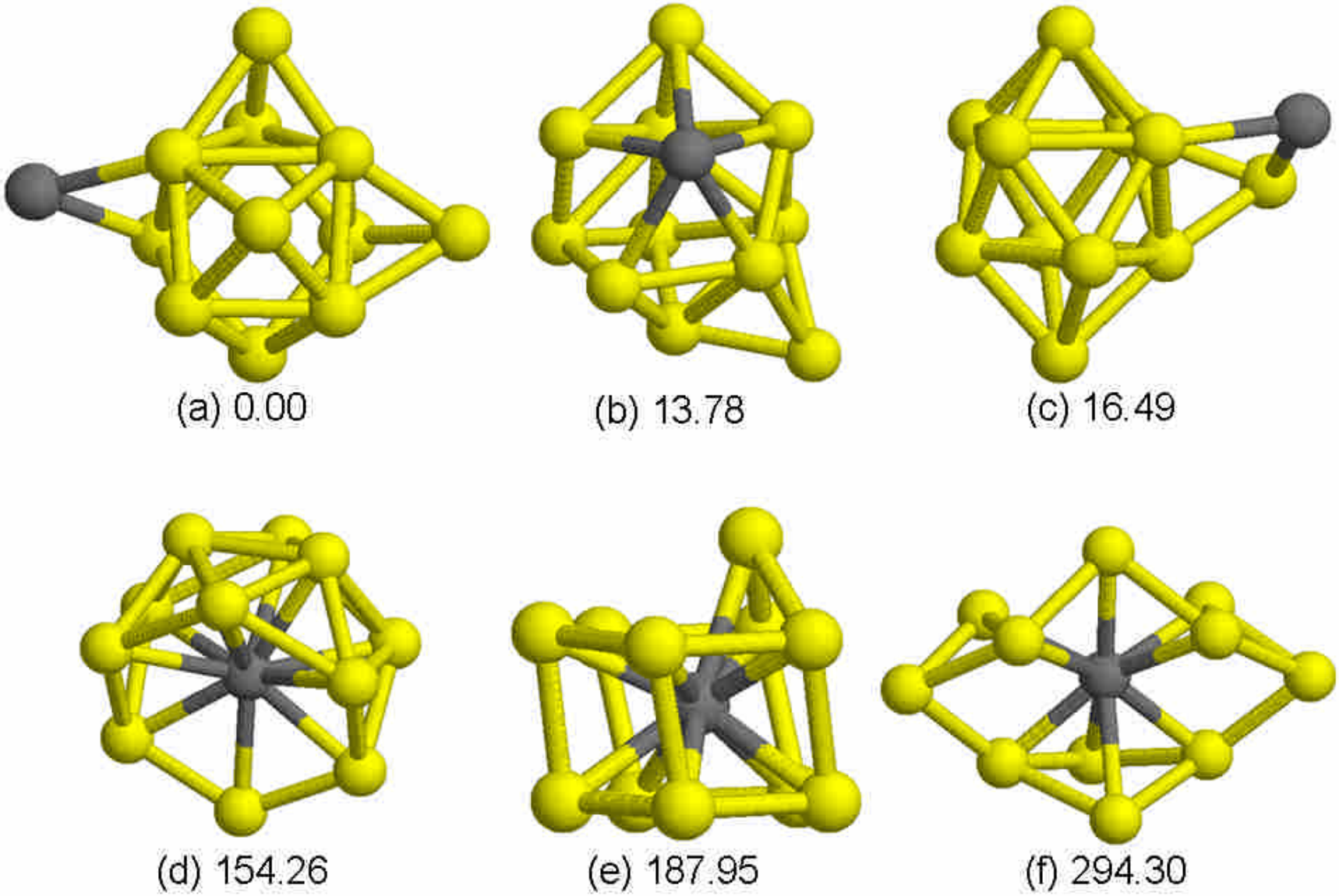
$AgSi_9$



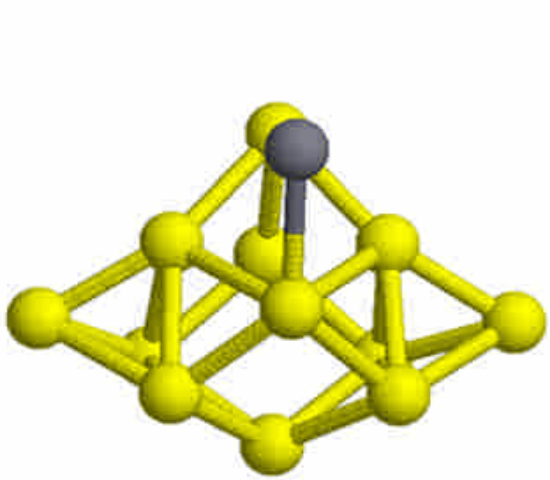
$AgSi_{10}$



$AgSi_{11}$

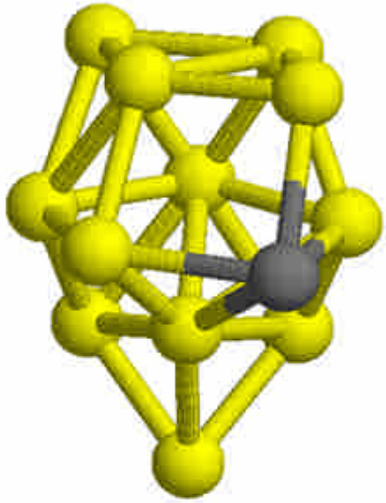


$AgSi_{12}$

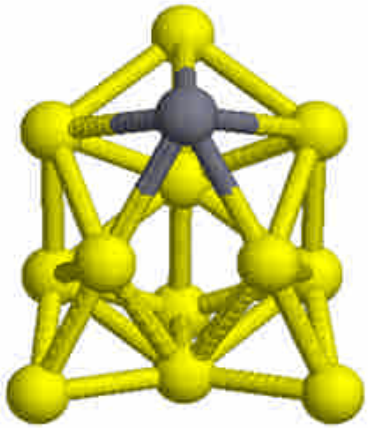


(a) 0.00

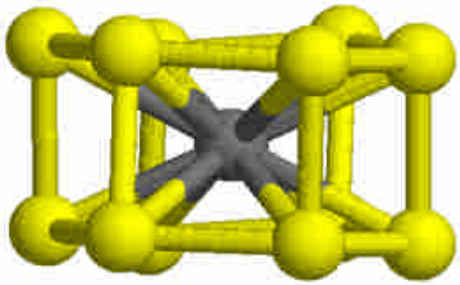
(b) 13.11



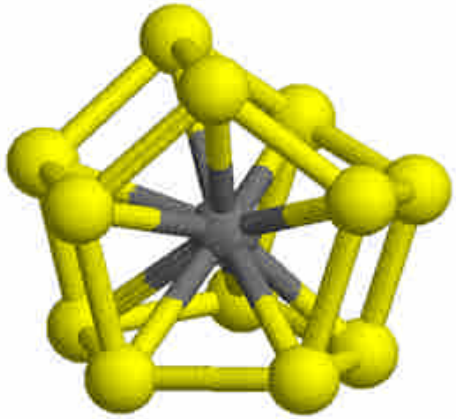
(c) 20.50



(d) 20.86

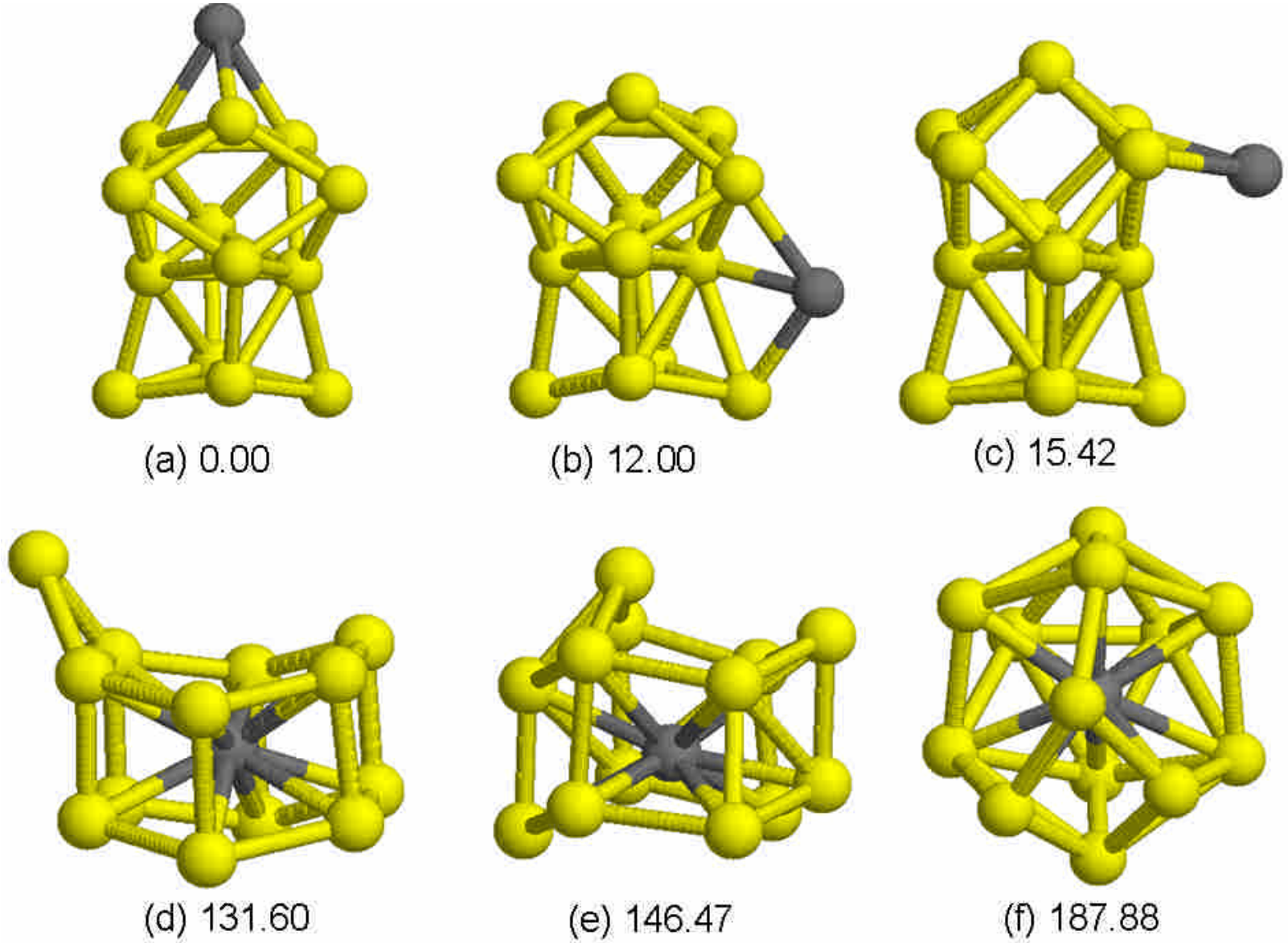


(e) 73.49

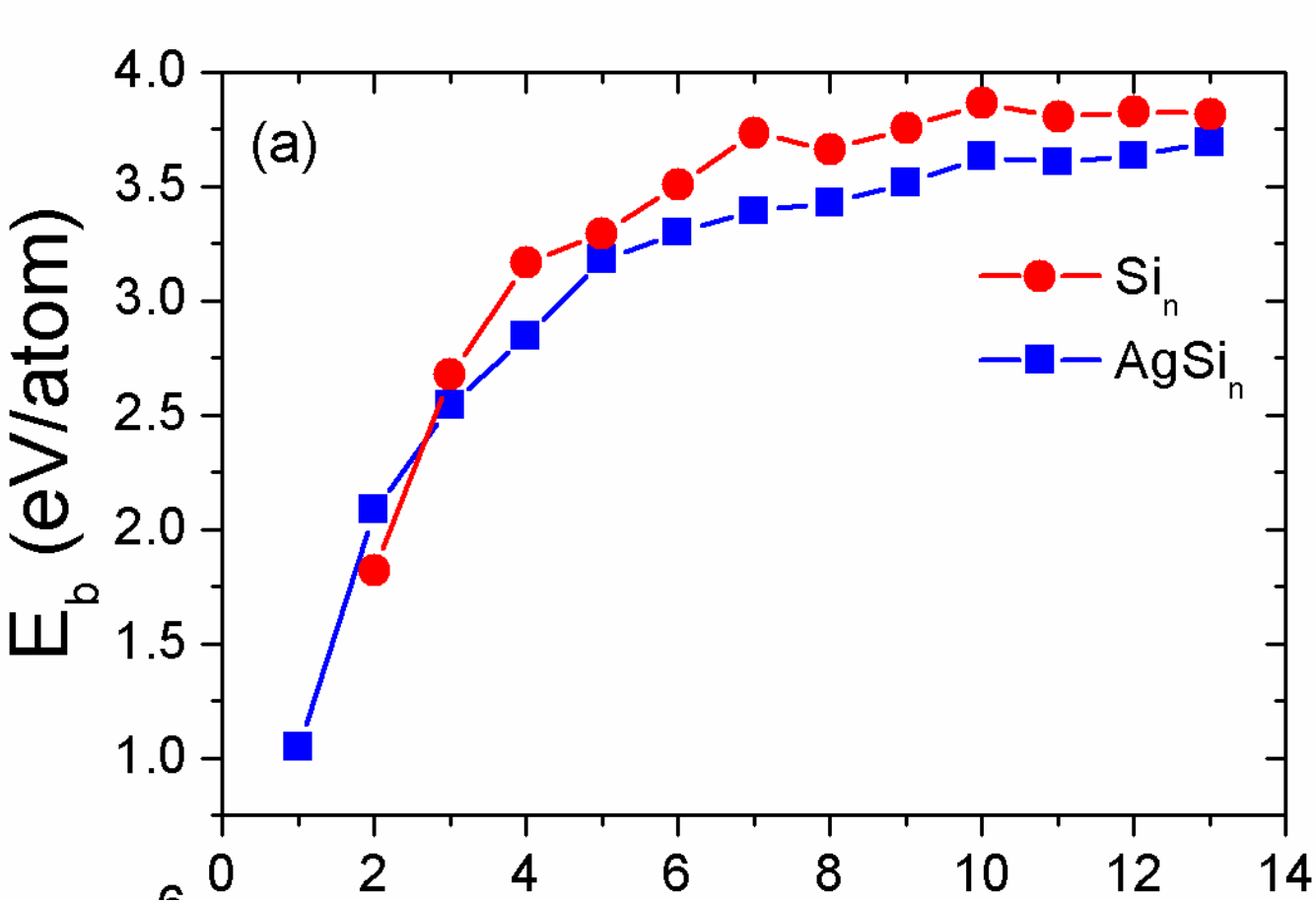


(f) 105.31

$AgSi_{13}$



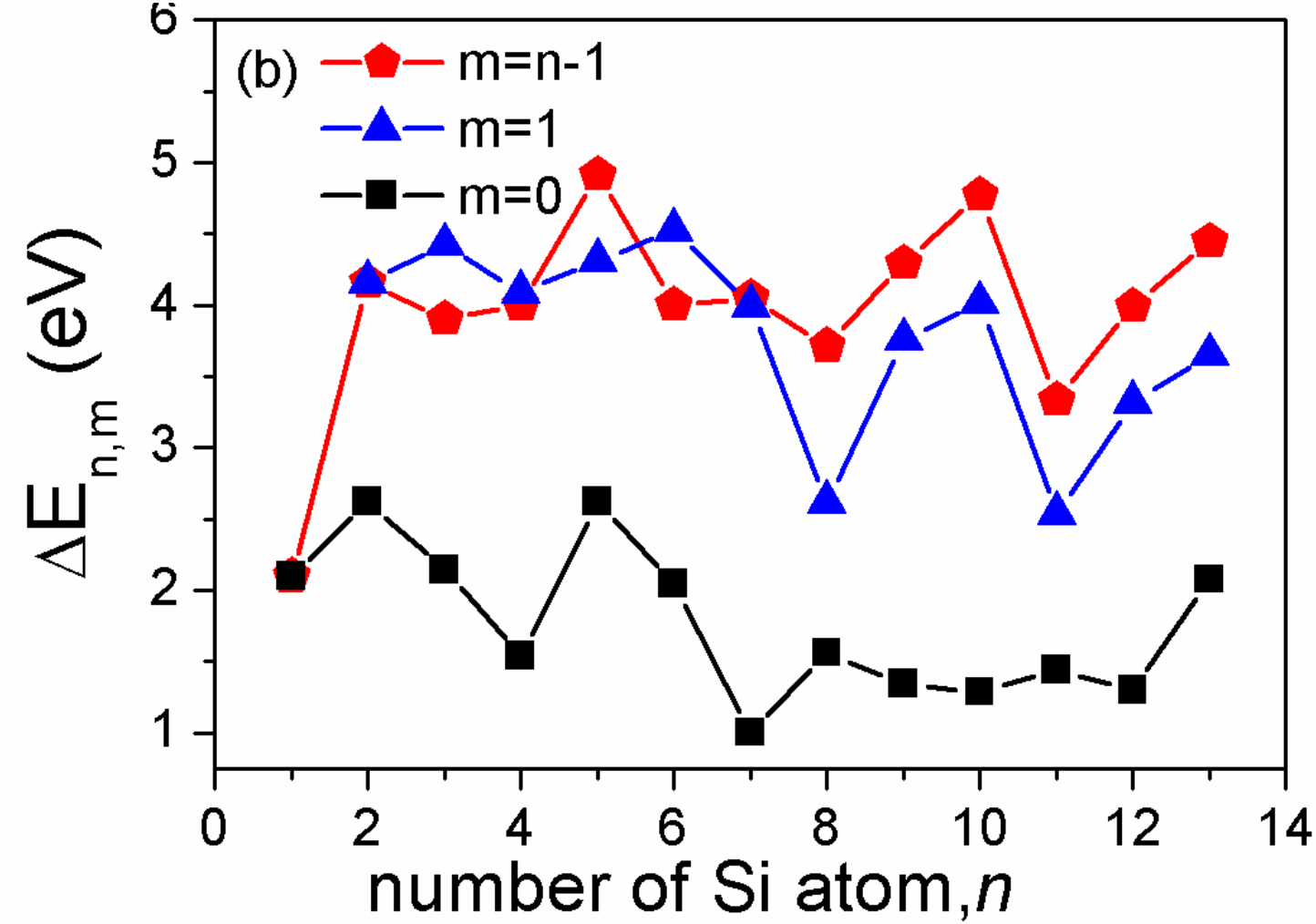
Binding Energy



$$E_b(AgSi_n) = -[E(AgSi_n) - E(Ag) - n \times E(Si)]/(n+1)$$

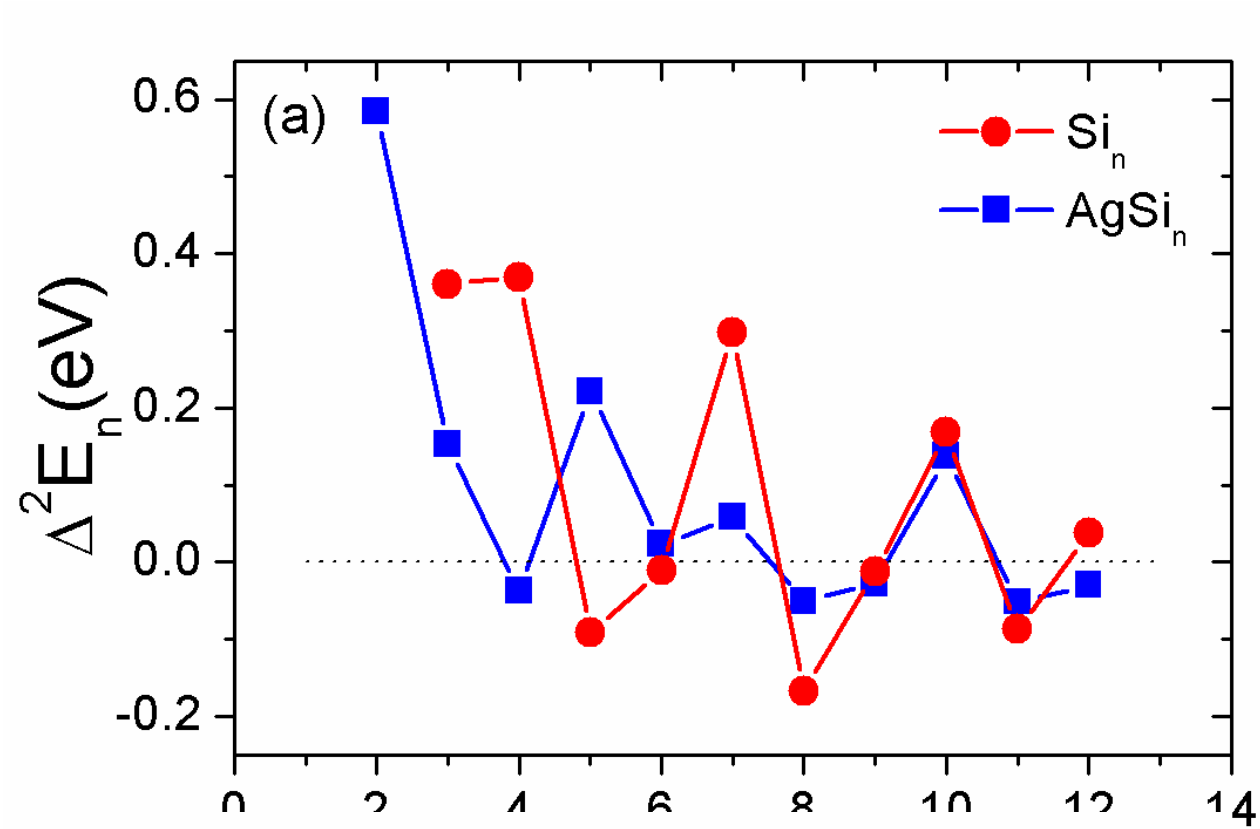
$$E_b(Si_n) = -[E(Si_n) - n \times E(Si)]/n,$$

Fragmentation energy



$$\Delta E_{n,m} = E(AgSi_m) + E(Si_{n-m}) - E(AgSi_n),$$

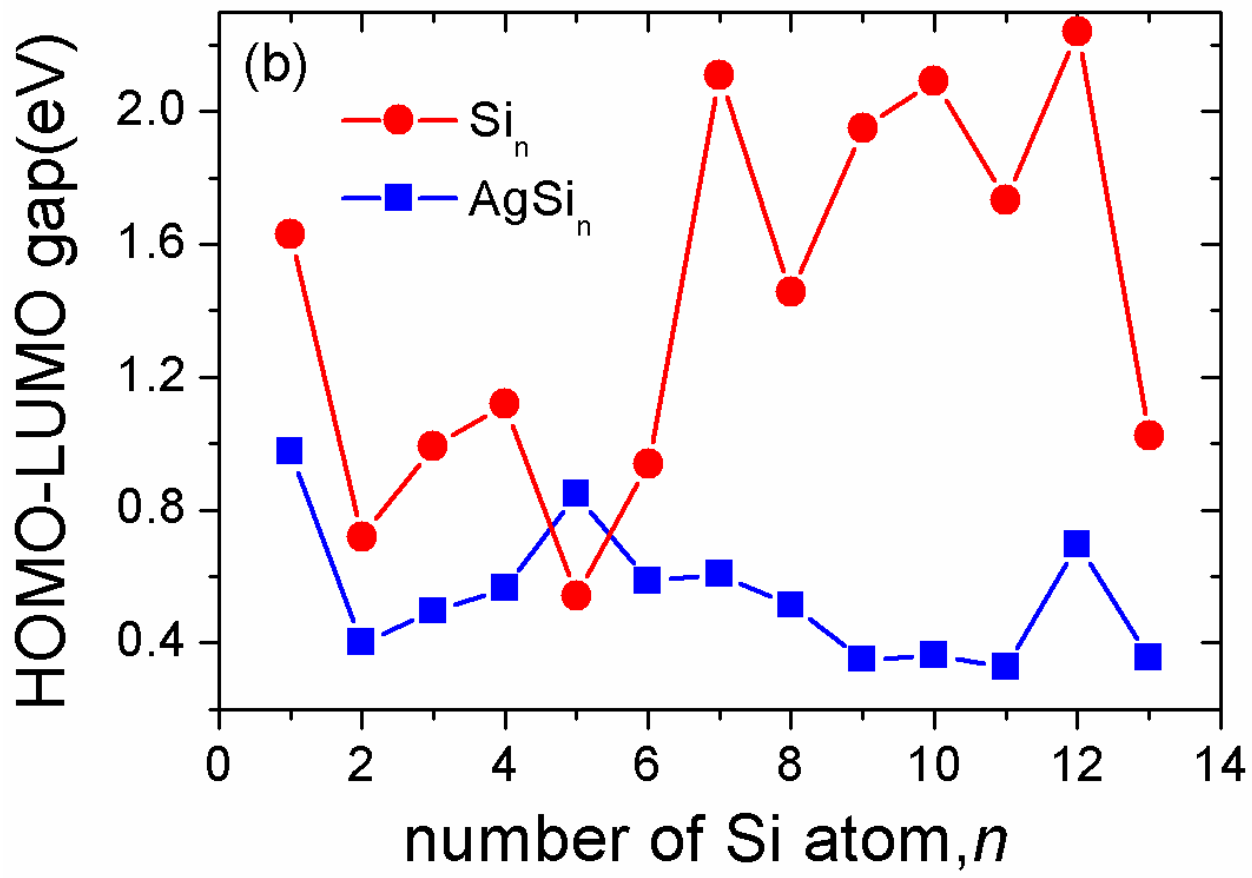
Second Difference in Binding Energy



$$\Delta^2 E(AgSi_n) = -2 \times E_b(AgSi_n) + E_b(AgSi_{n+1}) + E_b(AgSi_{n-1})$$

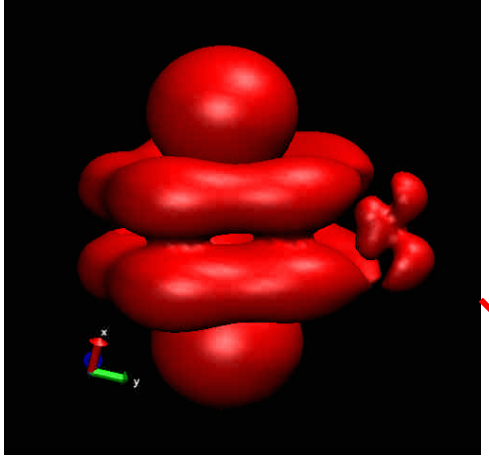
$$\Delta^2 E(Si_n) = -2 \times E_b(Si_n) + E_b(Si_{n+1}) + E_b(Si_{n-1}).$$

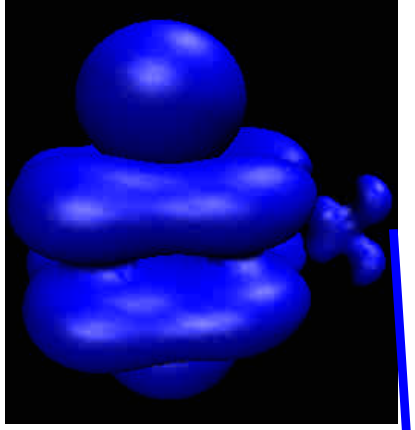
HOMO-LUMO gaps

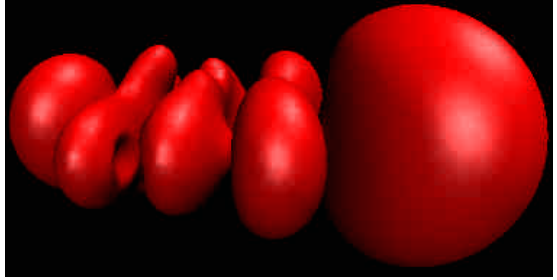


HOMO-LUMO gaps: the gaps between the highest occupied molecular orbital and the lowest unoccupied molecular orbital

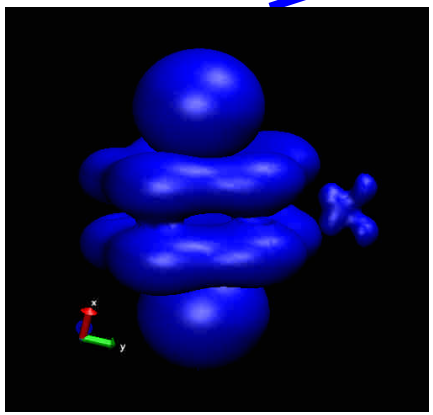
3D-total charge distribution iso-surface of $AgSi_7$ and $AgSi_{10}$

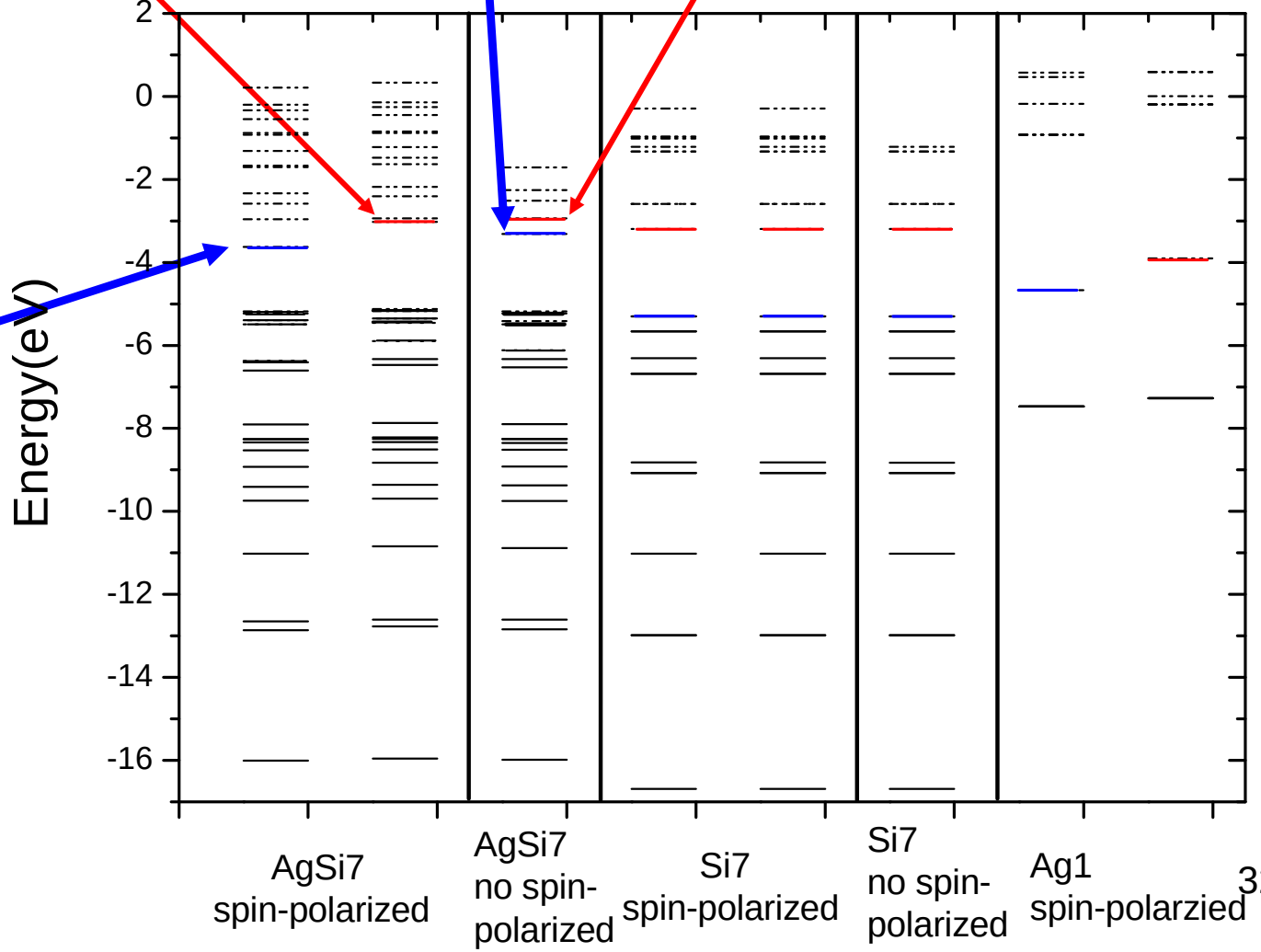






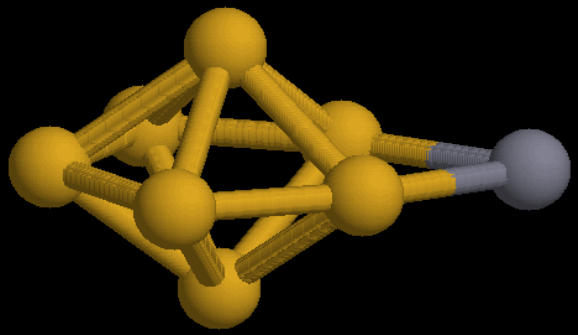
AgSi7 & Si7 & Ag1



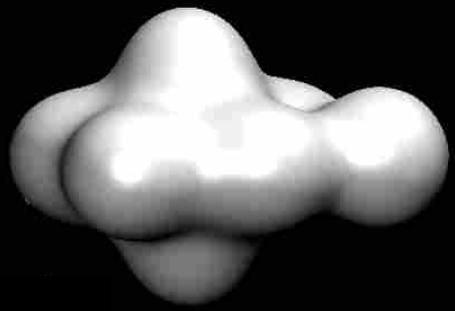


Spin-polarized

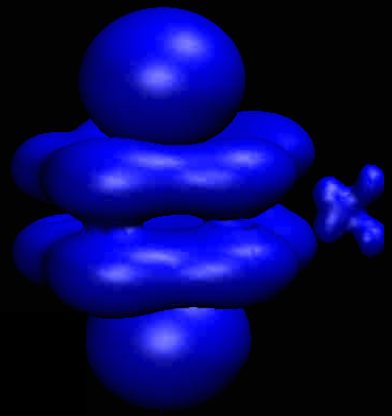
AgSi7



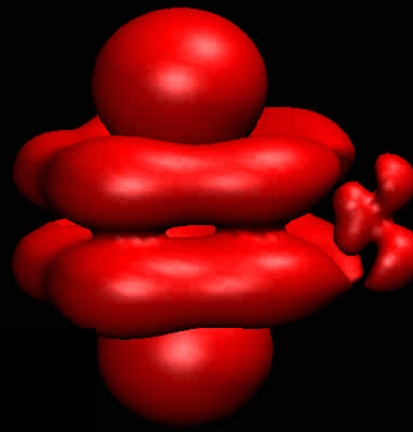
Total Charge



HOMO

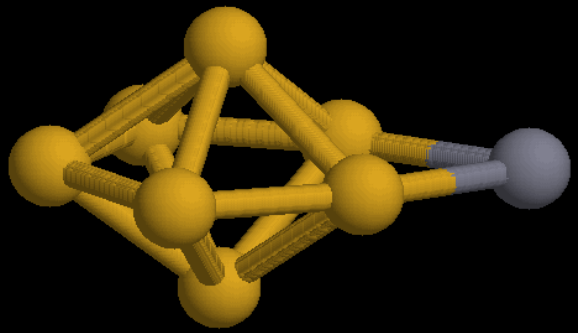


LUMO



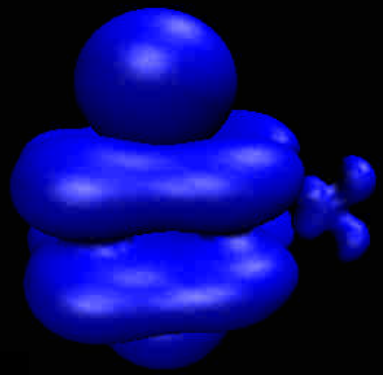
No Spin-polarized

AgSi7

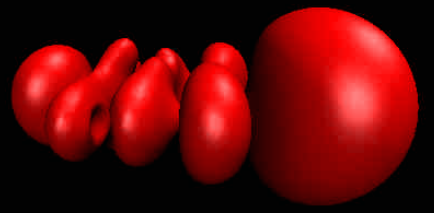


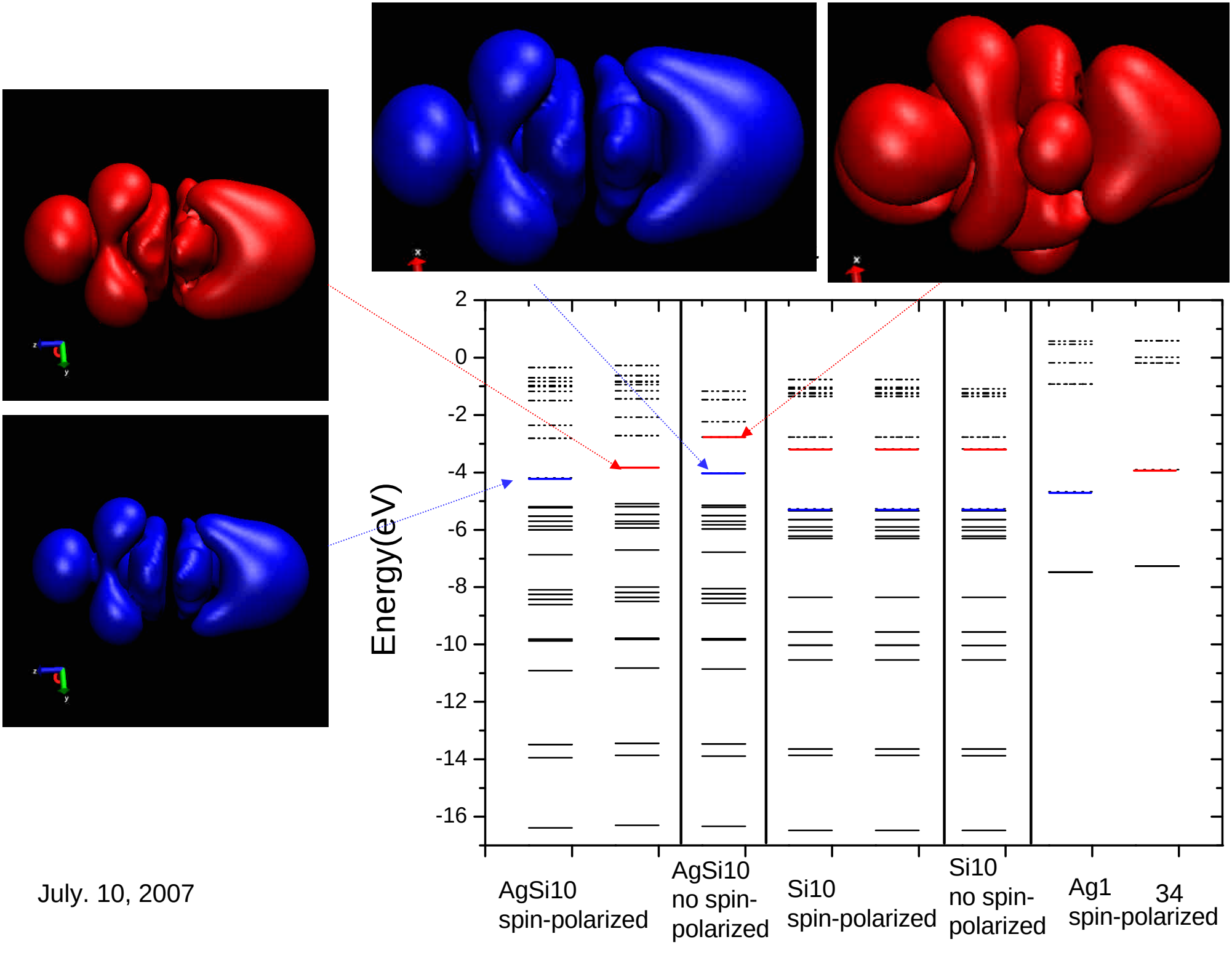
Total Charge

HOMO



LUMO

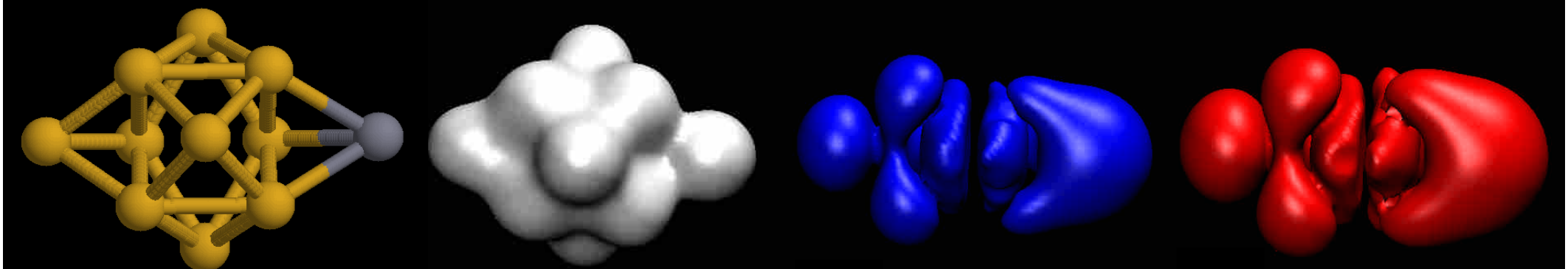



2
0
-2
-4
-6
-8
-10
-12
-14
-16
Energy(eV)
AgSi10
spin-polarized
AgSi10
no spin-
polarized
Si10
spin-polarized
Si10
no spin-
polarized
Ag1
spin-polarized
34

July. 10, 2007

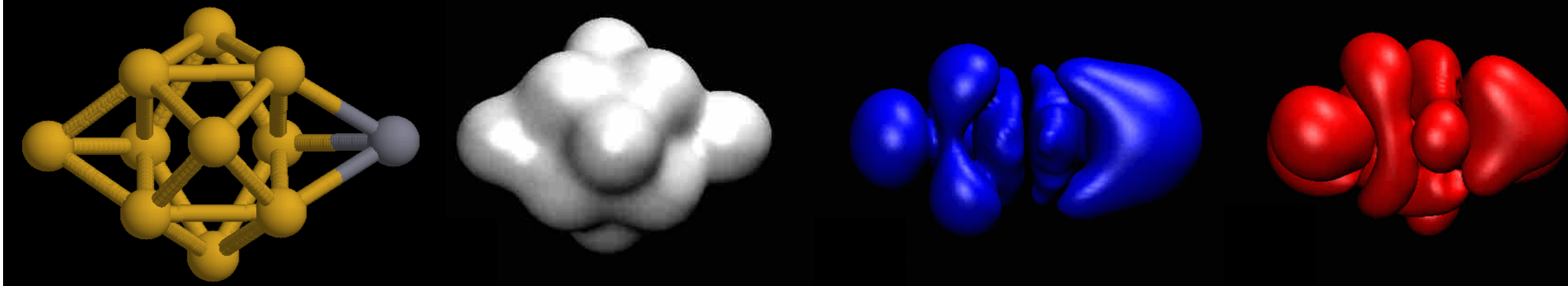
Spin-polarized

AgSi10 Total Charge HOMO LUMO



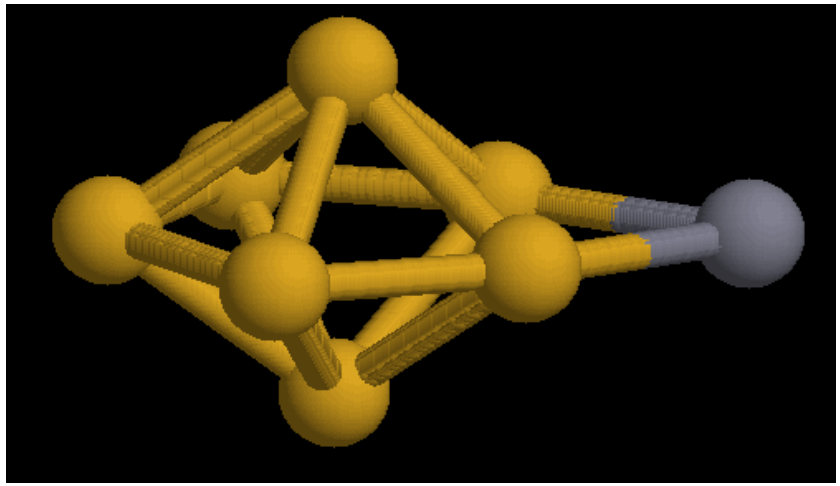
No Spin-polarized

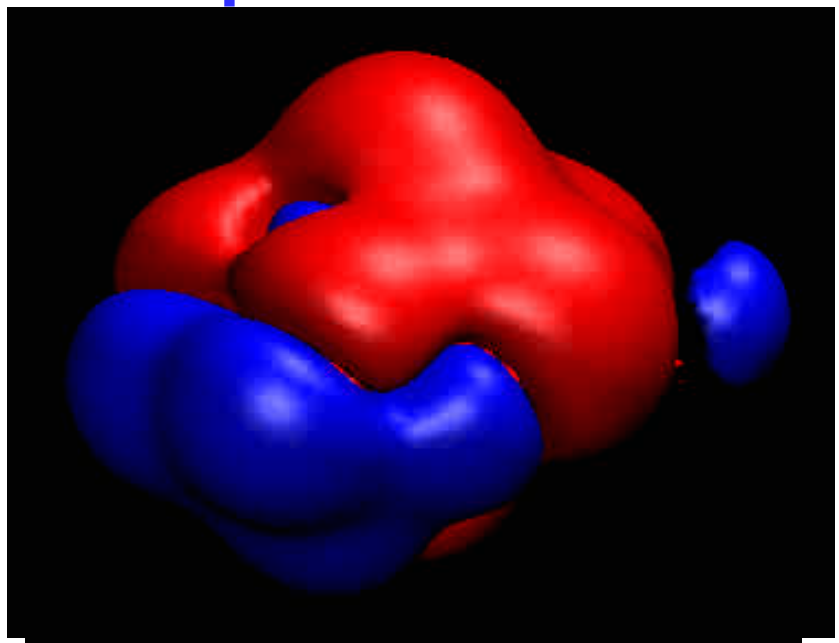
AgSi10 Total Charge HOMO LUMO



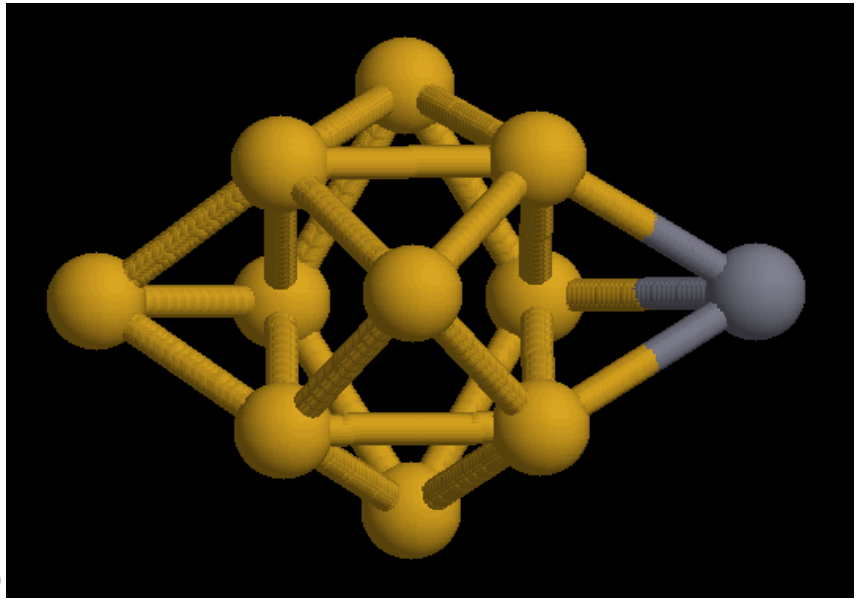
Charge transfer
accumulation and depletion

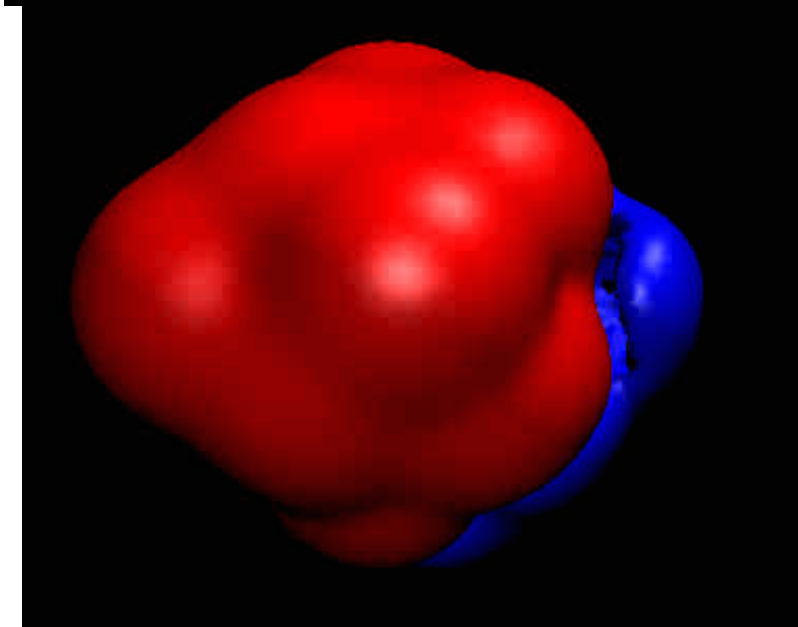
$AgSi_7$





$AgSi_{10}$





Conclusion

- Our results indicate that Ag atom prefers to cap the Si clusters rather than be embedded inside Si clusters.
- AgSi_{7} and AgSi_{10} are found to be two relatively stable clusters in agreement with experimental observations.
- In addition, for these clusters, doping leaves the inner core structure of the clusters largely intact. In contrast, the same study reveals that especially for relatively unstable clusters, substitution may compete with capping and may cause structural changes in the inner structure.
- Additionally, fragmentation analysis reveals that the primary pathway is through evaporation of a silver atom from a Ag-doped clusters, which is also in consistent with experimental data.
- Our data have also uncovered a secondary pathway for n > 7 (except n = 11) in which the Ag-Si cluster dissociate into Si_{7} and a smaller fragment AgSi_{n-7}. The AgSi_{11} cluster dissociates into a stable Si_{10} and a small fragment AgSi.
- Unfortunately, Ag-doped Si clusters are not best candidates for tailoring optical or magnetic properties.