Structure and Dynamics of Au Nanoclusters Using ANN Based Interatomic Potentials

by

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Discipline of Chemistry
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Introduction: Metal Nanoclusters

- Quantum size effect
- Surface to volume ratio
- Relativistic Effects


(PASC18)
Introduction: Metal Nanoclusters

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Graph showing the relationship between surface area per unit volume and radius of the particle.
Introduction: Metal Nanoclusters

- Metal nanoclusters
- Quantum size effect
- Surface to volume ratio
- Relativistic Effects


Graphs showing surface area per unit volume versus radius of the particle, nm. Graphs also show energy levels for different metal orbitals with and without relativistic effects.
Introduction: Thermal stability and Catalysis in Au nanoclusters

- Internal Energy Vs Temperature

Introduction: Thermal stability and Catalysis in Au nanoclusters

- **Internal Energy Vs Temperature**

- **Supported Au Nanoclusters**

Introduction: Thermal stability and Catalysis in Au nanoclusters

Internal Energy Vs Temperature

- Supported Au Nanoclusters
- Protected Au Nanoclusters

Methodology : Accurate Description of PES

- Potential energy surface (PES)
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- DFT and Empirical Potentials
Methodology: Accurate Description of PES

- Potential energy surface (PES)
  - Transition Structures
  - Second Order Saddle Point
  - Minimum for Product A
  - Second Order Saddle Point
  - Minimum for Product B
  - Valley-Ridge Intersection Point

- DFT and Empirical Potentials

- Machine Learning Potentials

Diagram:
- Atomic Positions → Descriptor
- Transformed Coordinates → Model
  (Neural Networks, Kernel ridge regression, Support Vector Machines)
- Energy, Forces
Methodology: FFNN for Single Component System

\[ E_i = \sum_{l=1}^{N_{hn}} W_{l1}^{23} \cdot f_l^2 \left[ Wb_l^2 + \sum_{k=1}^{N_{hn}} W_{kl}^{12} \cdot f_k^1 \left( Wb_k^1 + \sum_{j=1}^{N_D} W_{jk}^{01} \cdot S_{ij} \right) \right] \] (1)

\[ f = \frac{1}{1 + \exp(-y(i))} \] (2)

\[ E = \sum_{i=1}^{n} E_i \] (3)

Behler et al., PRL 98, 146401(2007).
Methodology: Training and Testing Network Weights

\[ RMSE(E) = \sqrt{\frac{1}{N_{ts}} \sum_{k=1}^{N_{ts}} (E_{k}^{DFT} - E_{k}^{NN})^2} \]  

\[ RMSE(F) = \sqrt{\frac{1}{N_{ts}} \sum_{k=1}^{N_{ts}} \left[ \frac{1}{3N_{atom}^k} \sum_{i=1}^{N_{atom}^k} \sum_{\alpha} \left( F_{k,i,\alpha}^{DFT} - F_{k,i,\alpha}^{NN} \right)^2 \right]} \]
Methodology: Spherical Harmonics Descriptor

Atomic density \( (\rho(\hat{r})) \)

\[
\rho(\hat{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{\kappa lm} e^{-\kappa r^2} f_c(r) Y_{lm}(\hat{r})
\]  

where \( Y_{lm}(\hat{r}) = N_{lm} P_{lm}(\cos \theta) \exp(i m \phi) \)

\[
f_c(r_{ij}) = \begin{cases} 
0.5[\cos \frac{\pi r_{ij}}{R_c} + 1] & \text{if } r_{ij} \leq R_c \\
0 & \text{if } r_{ij} > R_c
\end{cases}
\]

\( N_{lm} \) is Normalization constant
\( P_{lm} \) is Legendre Polynomial

Methodology: Spherical Harmonics Descriptor
Power Spectrum

- Angular Coefficients for each atom \( (S_i^{\text{ang}}) \):

\[
S_i^{\text{ang}} = P_{\kappa l} = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} c_{\kappa lm}^* c_{\kappa lm}
\]  

(7)

- Spherical harmonic coefficients \( (c_{\kappa lm}) \)

\[
c_{\kappa lm} = \sum_{i \neq j} e^{-\kappa r_{ij}^2} f_c(r_{ij}) Y_{lm}(r_{ij})
\]

(8)

- Radial coefficients for each atom:

\[
S_i^{\text{rad}} = \sum_{i \neq j} e^{-\eta r_{ij}^2} f_c(r_{ij})
\]

(9)

Methodology: Spherical Harmonics Descriptor

Bispectrum

- Power spectrum ($P_l$) is the Fourier transform of the autocorrelation function and gives the overall amplitude of the signal at a particular frequency.

\[
P_l = \sum_{m=-l}^{l} c_{lm}^* c_{lm}
\]  

(10)

- To extract maximum information from density projection = \textit{bispectrum}

\[
b_{ll_1l_2} = \sum_{m=-l}^{l} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} c_{lm}^* C_{mm_1m_2}^{ll_1l_2} c_{l_1m_1} c_{l_2m_2}
\]  

(11)
The rules followed in formulation of bispectrum are:

a) $l_1 + l_2 + l = \text{even}$  
b) $m_1 + m_2 = m$

For $l_1$ and $l_2$ running from 0 to 4, a possible number of 35 combinations are generated.

c) \textit{Bicoherence}. It signifies the fraction of energy present in signal at frequency $l$ due to coupling between $l_1$ and $l_2$.
\[
bicoh(l_1, l_2) = \sqrt{\frac{b_{l_1l_2}^2}{P_{l_1}P_{l_2}P_l}} \quad (12)\]

For $l_1$ and $l_2$ running from 0 to 4, a possible number of 15 combinations are generated.

Methodology: Spherical Harmonics Descriptor Bispectrum

**Figure**: Comparison of energy prediction from DFT, bispectrum, weighted and non-weighted ADF in power spectrum for a set of $Au_{147}$ clusters.
Feed Forward Neural Networks for Multicomponent Systems

\[
E_{i}^{Ag} = \sum_{l=1}^{N_{hn}} s W_{l1}^{23} . f_{l}^{2} \left[ s W_{l}^{2} + \sum_{k=1}^{N_{hn}} s W_{kl}^{12} . f_{k}^{1} \left( s W_{k}^{1} + \sum_{j=1}^{N_{in}} s W_{jk}^{01} . S_{ij}^{comb} \right) \right] (13)
\]

\[
E_{i}^{Au} = \sum_{l=1}^{N_{hn}} g W_{l1}^{23} . f_{l}^{2} \left[ g W_{l}^{2} + \sum_{k=1}^{N_{hn}} g W_{kl}^{12} . f_{k}^{1} \left( g W_{k}^{1} + \sum_{j=1}^{N_{in}} g W_{jk}^{01} . S_{ij}^{comb} \right) \right] (14)
\]
Angular Coefficients for each atom:

\[ S_{i,\text{mod}}^{\text{ang}} = P_{\kappa l} = \frac{4\pi}{2l + 1} \sum_{m=-l}^{l} c_{\kappa l m}^* c_{\kappa l m} \] (15)

Spherical harmonic coefficients \( (c_{\kappa l m}) \)

\[ c_{\kappa l m} = \sum_{i \neq j} w_{ij} e^{-\kappa r_{ij}^2} f_c(r_{ij}) Y_{lm}(r_{ij}) \] (16)

Radial coefficients for each atom:

\[ S_{i,\text{mod}}^{\text{rad}} = \sum_{i \neq j} w_{ij} e^{-\eta r_{ij}^2} f_c(r_{ij}) \] (17)

\[ E_{i,\text{mod}} = \sum_{l=1}^{N_{hn}} W_{l1}^{23} \cdot f_l^2 \left[ W_{b1}^2 + \sum_{k=1}^{N_{hn}} W_{kl}^{12} \cdot f_k^1 \left( W_{b1}^1 + \sum_{j=1}^{N_D} W_{jk}^{01} \cdot S_{ij} \right) \right] \] (18)
Methodology: Single Network for Multicomponent System
Atomic Forces

\[ F_{i,\alpha}' \text{ weighted} = - \sum_{N=1}^{\text{atoms input}} \sum_{k=1}^{\text{input}} \frac{\partial E_N'}{\partial S_{N,k}} \left( w_{\beta} \times \frac{\partial S_{N,k}}{\partial R_{i,\alpha}} \right) \] (19)

Q and Q’ are the descriptors for E and F’, respectively. \( F' = F^\text{weighted}_\alpha \) and \( E = E_{\text{cluster}} \). The block KF represents the global extended Kalman filter.
Application: Global Optimization of Au Nanoclusters

Figure: (a) GM of Au$_{34}$, (b) Au$_{34}$ core, (c) GM of Au$_{58}$, (d) Au$_{58}$ core

The empirical potentials have predicted $Au_{147}$ to be an icosahedron.

We found a new GM which is amorphous, lying 4eV below in energy than the icosahedron.

**Figure**: Geometries of $Au_{147}$ a) Icosahedron, b) GM.
Application 1: Probability of Au Nanoclusters

\[
p_{iso} = \frac{\exp \left( -\frac{\Delta E_{RP}^{iso}}{K_B T} \right) q_{rot}^{iso} q_{vib}^{iso}}{\sum_{iso} \exp \left( -\frac{\Delta E_{RP}^{iso}}{K_B T} \right) q_{rot}^{iso} q_{vib}^{iso}}
\]

(20)

Where \( \Delta E_{RP}^{iso} \) is relative potential energy of isomer from GM. \( q_{rot}^{iso} \) and \( q_{vib}^{iso} \) are rotational and vibrational partition function.

Table: Probability of 5 lowest isomers of Au\(_{34}\)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P_1(%)</th>
<th>P_2(%)</th>
<th>P_3(%)</th>
<th>P_4(%)</th>
<th>P_5(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>97.0</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>150</td>
<td>62.0</td>
<td>18.0</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>250</td>
<td>26.0</td>
<td>12.0</td>
<td>1.6</td>
<td>4.8</td>
<td>5.2</td>
</tr>
<tr>
<td>350</td>
<td>13.0</td>
<td>7.0</td>
<td>1.5</td>
<td>4.3</td>
<td>6.0</td>
</tr>
<tr>
<td>550</td>
<td>5.0</td>
<td>3.0</td>
<td>1.10</td>
<td>3.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>

In a core-shell structure, the fluxionality can be due to a dynamic surface or a dynamic core. Order parameters used to study fluxionality:

- Average bond length fluctuation
- Volume variation
- Root mean square distance
- Atomic equivalence index

Average bond length fluctuation

Figure: Average bond length fluctuations of $Au_{147}$ at 400K
Peaks in heat capacity plot for $\text{Au}_{34} = 550$ K, 970 K and for $\text{Au}_{58} = 955$ K.

Figure: Heat capacity plots for (a) $\text{Au}_{34}$ and (b) $\text{Au}_{58}$.

Application: Melting in Au Nanoclusters
Caloric curves and Phase coexistence in Au Nanoclusters

Figure: Caloric curves of NVE ensemble (a) Au$_{34}$ (b) Au$_{58}$

Figure: Low lying isomers of (a) Au\textsubscript{55} (b) Ag\textsubscript{5}Au\textsubscript{50} (c) Ag\textsubscript{13}Au\textsubscript{42} (d) I,II,III are Ag\textsubscript{28}Au\textsubscript{27} and, IV and V are GM of Ag\textsubscript{42}Au\textsubscript{13} and Ag\textsubscript{55}.

Figure: Heat capacity curves for (a) Au$_{55}$, (b) Ag$_{13}$Au$_{42}$, (c) Ag$_{28}$Au$_{27}$, (d) Ag$_{55}$

Application 3: Structural Trends in Au-SH Nanoclusters

Figure: Global Minimum Structures for \((\text{Au})_n(\text{SH})_m\) (n=15,25) Nanoclusters
### Table: Probability of 4 lowest isomers of thio-protected $\text{Au}_{38}$ to $\text{Au}_{13}$ at 400 K

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$P_1(%)$</th>
<th>$P_2(%)$</th>
<th>$P_3(%)$</th>
<th>$P_4(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}<em>{25}(\text{SH})</em>{18}$</td>
<td>100</td>
<td>5.39</td>
<td>5.05</td>
<td>5.18</td>
</tr>
<tr>
<td>$\text{Au}<em>{25}(\text{SH})</em>{10}$</td>
<td>4.84</td>
<td>3.74</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>$\text{Au}<em>{15}(\text{SH})</em>{13}$</td>
<td>12.5</td>
<td>5.84</td>
<td>3.74</td>
<td>3.74</td>
</tr>
<tr>
<td>$\text{Au}<em>{15}(\text{SH})</em>{8}$</td>
<td>1.08</td>
<td>1.52</td>
<td>1.16</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Conclusions

- Modelling ANN based inter-atomic potentials with DFT accuracy. (a) $Au_n, \ n=13-58$ (b) Ag-Au nanoalloys $((AuAg)^{55})$ (c) $(Au)_n(SH)_m, \ n=13-38$

- The structure, thermal stability of Au and $(AuAg)^{55}$ and $(Au)_n(SH)_m$ nanoclusters and chemical ordering in $(AuAg)^{55}$ nanoclusters provides fundamental understanding to design novel catalysts based on Au.

- The study based on probability allows one can observe keenly, the properties at finite temperature for finite sizes can be expressed as ensemble average of most probable isomers.

- Structure and thermal stability of $(Au)_n(SH)_m$ nanoclusters shows a monotonic dependence of SH compositions on Au nanoclusters.
Thank you