ABCluster: Global Optimization of Atomic and Molecular Clusters

Jun Zhang
Jan. 5, 2016
Content

• What is a Cluster
• Global Optimization: Principles and Applications
• Conclusions
What is a Cluster?
What is a Cluster?

- Cluster: an aggregate composed of a few to several million identical or different structural units like atoms and molecules.

Applications

- Crystal growth ($Ar_n$)
- Novel materials ($Pt_{13}$)
- Solvation structure ($Na^+ (H_2O)_n$)
- Catalysis ($Au_n$)
- Liquid structure ($(CH_3OH)_n$)
- Theoretical model ($pK_a, \Delta H$)
Stable Structure of a Cluster

- Potential energy surface (PES): a stable structure should be a minimum!
Stable Structure of a Cluster

- It is believed that, at room and biological temperature, molecules exist in the geometry of the **global minimum (GM)** on the free energy surface.
- At low temperature, one can omit entropy effect, thus considering a PES is sufficient.
- The most stable forms of proteins, alloys, polymers, ... Are the GM!

At 298 K, the ratio between two substance differing by 1 kcal/mol:

\[
\exp\left(\frac{1000}{1.99 \times 298}\right) = 5.42
\]
Determination of a Local Minima

- Mathematically, the determination of the minima of a function is an optimization procedure.
- **Local optimization** in computational chemistry is a very routine task.
- Confirmation of a LM: zero gradient.

\[
y = x^2 - 2x + 1
\]

\[
\nabla y \bigg|_{x=1} = (2x - 2) \bigg|_{x=1} = 0
\]
Determination of a Local Minima

Start with a random structure, we can always arrive at a local minimum.
Determination of the Global Minimum

- **Global optimization**: Much more difficult!
- We can never make sure that a minimum is a global one!

\[ y = x^4 - \frac{19}{2} x^3 + \frac{63}{2} x^2 - 43x + 20 \]

\[ \nabla y \bigg|_{x=1.3563} = 0 \]
\[ \nabla y \bigg|_{x=3.5117} = 0 \]

We cannot tell which LM is lower without doing the actual calculation!
Determination of the Global Minimum

Start with a random structure, we cannot always arrive at a global minimum!
More serious, we never know there is another “global minimum” in a mysterious place…
Global Optimization of Clusters

• No trivial condition for identifying a GM.
• The number of LMs increases \textit{exponentially} with the cluster size!

The number of isomers of \((\text{H}_2\text{O})_N\) increases as \((3/2)^N\)

\[
\begin{align*}
(3/2)^{20} &= 3325 \\
(3/2)^{30} &= 191751
\end{align*}
\]

L. Pauling, JACS, 1935, 57:2680
Global Optimization of Clusters

- Consider a peptide with 100 rotatable bonds.
- Assume each dihedral angle has 10 possibilities, the total number of conformations is $10^{100}$
- Folding this peptide by HUMAN BEING to the GM requires $10^{87}$ years!
- Cell accomplishes this in several seconds!

Levinthal’s Paradox

Global Optimization of Clusters

• The GM is very sensitive to the interactions of the cluster.

Morse model cluster, $N = 40$
Different force range leads to completely different GM
Global Optimization of Clusters

\textbf{Ag}_{38}

\textbf{Cu}_{38}

\textbf{Ag}_{32}\textbf{Cu}_{6}
Global Optimization of Clusters

- A shorter-ranged and multi-modality potential leads to a more complex PES!
- With so many LMs, the PES can be very rugged!
Global Optimization of Clusters

- We will always **smooth** the PES before optimization to reduce the roughness.
- This can remove the **barriers** alone the downhill movement of a funnel.
Algorithms for Global Optimization

- **Deterministic algorithms**: no robust, general ways. “Exhaustion” is impossible for most cases.
- **Non-deterministic algorithm**: one can locate the GM with some probability. It is the practical one.

**Evolution Algorithms**
- Genetics algorithm
- Differential evolution

**Swarm Intelligence**
- Particle swarm optimization
- Artificial bee colony algorithm
Swarm Intelligence
The ABC Algorithm

- Artificial Bee Colony (ABC) algorithm: an easy but powerful global optimization algorithm!
- A bee colony tries to find the best food source, just like we want to find the global minimum of a cluster.
- So we mimic the foraging behavior of honey bees.

D. Karaboga, Technical Report TR06, Erciyes University, 2005
The ABC Algorithm

- **Employed Bees**: Do the first exploration of the structures. (Random Noise and Fluctuation)
- **Onlooker Bees**: Based on the information obtained by employed bees, refine the structures. (Positive Feedback)
- **Scout Bees**: Detect if there are “bad” structures that do not contribute to the improvement of the results, discard them and generate new ones. (Negative Feedback and Memory Effect)

ABC algorithm is self-organizing!

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Algorithm Parameters

Parameters:
• $SN$: number of trail solutions
• $g_{\text{max}}$: the maximal number of search
• $g_{\text{limit}}$: the update frequency

Energy:
• Force field parameters
• Quantum chemistry
Initialization

Step 1: Initialization: with SN random $X_i^{1}$’s

$X$: cluster geometry

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Employed Bee Search

Step 2: EM search: for each $X_i^g$, a $V_i$ is obtained from other $X_j^g$’s by trigonometric mutation operator, and $X_i^{g+1}$ is updated by greedy condition.

$$
V_i = \frac{1}{3} \left( X_{k_1}^g + X_{k_2}^g + X_{k_3}^g \right) \\
+ (p_2 - p_1)(X_{k_1}^g - X_{k_2}^g) \\
+ (p_3 - p_2)(X_{k_2}^g - X_{k_3}^g) \\
+ (p_1 - p_3)(X_{k_3}^g - X_{k_1}^g)
$$

greedy condition updating

$$
X_i^{g+1} = \begin{cases} 
V_i, & \text{if } \tilde{U}(V_i) < \tilde{U}(X_i^g) \\
X_i^g, & \text{otherwise}
\end{cases}
$$

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Step 3: OL search: for “good” $X^g_k$ from tournament selection, a $V_k$ is obtained from other $X^g_j$'s by ABC/2, and $X^{g+1}_k$ is updated by greedy condition.

Onlooker Bee Search

ABC/2

$$V_i = \begin{cases} 
X^g_k + F \left( X^g_{k_1} + X^g_{k_2} - X^g_{k_3} - X^g_{k_4} \right), & \text{if } \eta < 0.5 \\
X^g_{\text{best}} + F \left( X^g_{k_1} + X^g_{k_2} - X^g_{k_3} - X^g_{k_4} \right), & \text{otherwise}
\end{cases}$$

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Scout Bee Search

Step 4: SC search: each $X^g_i$ that does not change in the last $g_{\text{limit}}$ cycles is updated with a random $X^{g+1}_i$

This introduces memory effect into the algorithm, which is an important character for intelligent algorithm!

$g_{\text{limit}} = 5$

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
The EM-OL-SC search repeats until $g_{\text{max}}$ is reached!
ABCluster: ABC for Clusters

- An easy, powerful, black-box, and free software for the global as well as local optimization of clusters!

One can download ABCluster freely from:

ABCluster: Download  Gallery  Stories

ABCluster 1.5 available! Several important improvements:

- A component cg-optimizer is added to support the anistropic, coarse-grained particles, including electric multipole interaction and Paramonov-Yaliraki potential.
- The component rigidmol-optimizer supports 1D, 2D and 3D periodic boundary conditions.
- New modified Sutton-Chen and extended Lennard-Jones potential are supported.
- A new keyword surface is added to lego for better supporting surface absorption.
- The output of isomer and lego are optimized.

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
**ABCluster**: ABC for Clusters

**Applications**

- Ionic cluster
  - Oxides, silicates, silica-based glasses
  - Fullerene cluster
  - Metal and alloy clusters
  - Microsolvation clusters
  - Nonpolar clusters
  - Biological molecular clusters
- Can work with any empirical potentials and quantum chemical programs

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Application: MgO Cluster

- MgO cluster
- With Born-Mayer potential
- With different formal $Q$, the GM changes from lattices to tube to cage.
Application: Metal and Alloy Cluster

- With Gupta many-body potential

  - $\text{Pt}_{38}$: with a standard FCC structure
  
  Pt, La, Ag, … typical close-packed structure

  - $\text{Zn}_{38}$: with a disordered structure
  
  Zn, Ca, Au, … typical disordered, amorphous structure

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Application: Metal and Alloy Cluster

- With Gupta many-body potential

$$\text{Cu}_8\text{Ag}_4\text{Au}_7$$  $$\text{Ag}_{32}\text{Cu}_6$$

Oxygen reduce activity

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Application: Metal and Alloy Cluster

- With Gupta many-body potential

Au$_{42}$Pd$_{13}$

Pd-core-Au-shell structure!

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
Application: Metal and Alloy Cluster

“Janus” Structure

$\text{Au}_{13}\text{Pd}_{42}$

J. Zhang, M. Dolg, PCCP, 2015, 17:24173
A. Bruma, etc. Nanoscale 2013, 5:646
Application: Water Clusters

- Water clusters are of **fundamental** importance in science.
- And also a great **challenge** in global optimization.
- ABCluster can always find the correct GM.
Application: Hydrated Alkali Cations

- From Na$^+$, K$^+$ to Cs$^+$, large coordination number is observed.

\[ \text{Na}^+{(H_2O)}_{20} \quad \text{K}^+{(H_2O)}_{20} \quad \text{Cs}^+{(H_2O)}_{20} \]
Application: Hydrated Anions

• Anions have completely **different** interaction modes from cations.
Application: Hydrated Anions

- Anions can significantly reduce the number of dangling OH bonds.

\[ \text{SO}_4^{2-}(\text{H}_2\text{O})_{20} \]

J. Zhang, M. Dolg, PCCP, 2016, 18:3003

No OH peak!
Application: Polar with Nonpolar

- Water can just “wet” some nonpolar molecules.

\[(\text{H}_2\text{O})_{10}@\text{Graphene}\]

\[\text{CH}_4(\text{H}_2\text{O})_{20}\]

- Methane clathrate is not the global minimum!

J. Zhang, M. Dolg, PCCP, 2016, 18:3003
Application: Charged but Hydrophobic

- Guanidinium (Gmd$^+$): one strongest protein denaturant!
- It is charged, as Na$^+$. However, it is recognized as one of the weakest hydrated molecule: No hydration shell were detected at all!
Application: Charged but Hydrophobic

- Our result explains the fact that why arginine is more buried inside the protein instead of exposing on the surface, like other positive charged residues.
- An internal arginine residue offers charge needed in the interior of a protein.
Application: CH$_3$CN with Cl$^-$

J. Zhang, M. Dolg, PCCP, 2016, 18:3003
Application: CH$_3$CN with Cl$^-$

J. Zhang, M. Dolg, PCCP, 2016, 18:3003
Application: CH$_3$CN with Cl$^-$

Cl$^-$(CH$_3$CN)$_{33}$

Surface solvated!

J. Zhang, M. Dolg, PCCP, 2016, 18:3003
Application: Dispersion Clusters

(\text{CH}_4)_{13}

(\text{CO}_2)_{13}

(C_6H_6)_{13}

J. Zhang, M. Dolg, PCCP, 2016, 18:3003
Application: With Quantum Chemistry

- ABCluster can work with all kinds of Quantum Chemical Programs!
- \( \text{Al}_3\text{O}_4 \): ABCluster+Gaussian09, B3LYP/6-31g(d)
Application: With Quantum Chemistry

- Search the possible active species.
- Using ABCluster, we get a series of possible isomers of the activator, and search the transition state...

\[ \text{H}_2\text{O}/\text{CH}_4 \rightarrow \text{HO·}/\text{CH}_3· \]

Hydrogen Abstract Reaction

Future Development

- Increasing the efficiency of Alloys
- Most Challenging: very delocalized INORGANIC cluster!

Obtain ABCluster!


ABCluster: Download  Gallery  Stories

ABCluster 1.5 available! Several important improvements:

- A component cg-optimizer is added to support the anisotropic, coarse-grained particles, including electric multipole interaction and Paramonov-Yaliraki potential.
- The component rigidmol-optimizer supports 1D, 2D and 3D periodic boundary conditions.
- New modified Sutton-Chen and extended Lennard-Jones potential are supported.
- A new keyword surface is added to lego for better supporting surface absorption.
- The output of isomer and lego are optimized.
THANK YOU!