# Global Optimization of Lennard-Jones clusters by Basin-Hopping.

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## ABSTRACT

Atomic clusters comprising a few to tens of atoms have vast configurational spaces. This large configurational space makes discovering the most stable configurations of these clusters extremely challenging. Global optimization of these clusters is a key challenge in computational chemistry and condensed matter physics, with nanotechnology and materials science applications. Finding the most stable configuration of a cluster requires searching for the global minimum of the potential energy surface (PES), a task that becomes increasingly complex as the number of atoms grows due to the rising number of local minima. Lennard-Jones (LJ) clusters serve as useful test systems since they provide a simplified model of atomic interactions.

I'll execute the basin hopping algorithm, which is a global optimization technique that reduces the PES for every configuration into a local minimum. This approach collapses energy barriers, which makes it simpler to find the most stable structure. The algorithm incorporates Monte Carlo steps with local optimization, which enhances the search for the global minimum.

My objective is to reproduce and expand upon the work of Wales et al.1 by examining LJ clusters of 40 atoms or fewer. I will compute the lowest energy configuration of my different clusters. This effort should help confirm the usefulness of the basin-hopping method, and the code developed will further the effort in research on elastically adaptable materials with complex configurational landscapes.

# 1. INTRODUCTION

Global optimization is the process of finding the optimal solution to a problem, either a global maximum or minimum, from all possible solutions, including those that are good, or optimal but not as good a value as would be anticipated. In contrast to local optimization, which is trapped in nearby peaks or valleys, global optimization examines all possible solutions and ensures the optimum one.[1]

Atomic clusters are a limited number of atoms, typically from a few to several hundred. They fall between molecules and bulk material and have distinct physical, chemical, and structural features that are commonly distinct from bulk material properties and display considerable their counterparts. Knowing their structures is significant for various applications in relation to nanotechnology, catalysis, materials science, and molecular electronics.

As far as cluster science is concerned, one of the most important problems one has to solve is to determine the most stable structure, which is the most reasonable solution and the global minimum of the potential energy surface (PES) of the system. But the potential energy landscape of atomic clusters is rough, complex, and multidimensional, with permanent local minima, which best describes the rugged cases for global minimum optimization for large systems. For example, PES of the 147-atom cluster possesses the order of $10^{60}$ local minima.[2]

Fig. 1 illustrates, disconnectivity graph for the LJ 38 cluster. there are so many local minima points. Each node is displaying one local minimum point, and finding the global minimum for this kind of structure is very challenging. So, in atomic cluster research, global optimization is vital to forecast stable structures and identify their intrinsic properties. So, the basin hopping method is proposed by Wales and Doye.[3]

Among these clusters, LJ38 is especially hard to test with smaller clusters, which tend to favor highly symmetrical icosahedral configurations. LJ38 has a more complicated energy landscape. It possesses two dominant rivaling structures — an incomplete icosahedron (a low-energy local minimum) and a truncated octahedron (the genuine global minimum). Sizable barriers split these structures and render it nearly impossible for elementary algorithms to spot the appropriate answer.[4, 5]

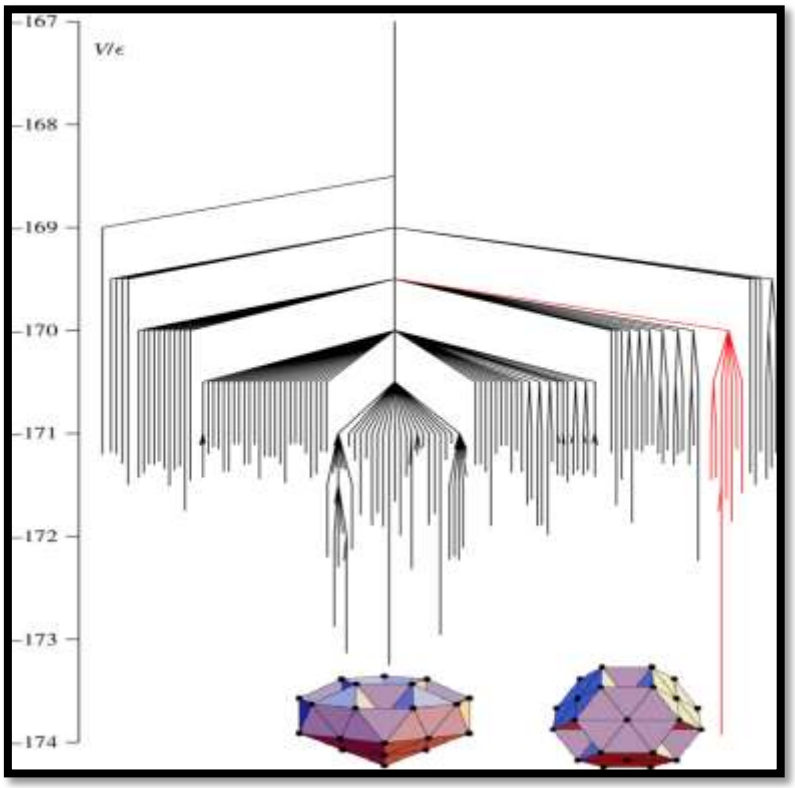



Fig.1: Disconnectivity graph for the LJ 38 cluster. In this case, there are two competing morphologies separated by a high barrier, corresponding to an incomplete Mackay icosahedron and a truncated octahedron. Branches of the graph associated with minima based on the octahedron are coloured red. The energy is in units of e, which is the pair well depth for the Lennard-Jones potential

Lennard-Jones (LJ) clusters are model systems of atoms that interact via the Lennard-Jones potential, a simple but effective description of van der Waals interactions. The LJ potential captures the key aspects of atomic interactions: short-range repulsion and long-range attraction. It is mathematically given by:[6]

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where:

- ε is the depth of the potential well (representing long-range attraction),
- σ is the distance at which the potential is zero,
- r is the separation between two atoms.

Throughout the simulation, reduced units are used, i.e., ε=σ=1.

The graph of the LJ potential is shown in Fig. 2.
The simplicity of the LJ potential, along with the availability of well-characterized global minima for clusters containing up to several hundred atoms, makes LJ clusters ideal test cases for optimizing and developing algorithms.

Therefore, this system is commonly used for testing optimization algorithms in simulations. The identification of global minima for LJ clusters up to *N=147* atoms has been achieved through the cumulative efforts of various researchers,[7, 8] providing a valuable benchmark for algorithm development.

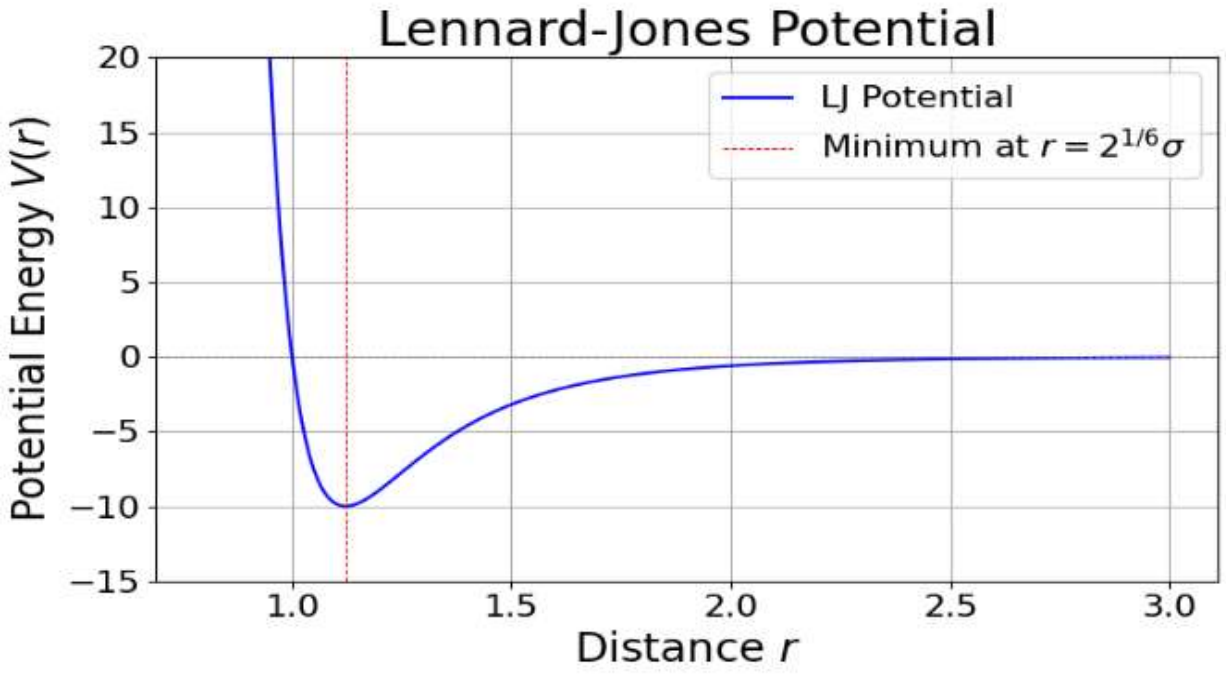



Fig. 2: Lennard-Jones potential energy curve illustrating the interaction between two neutral atoms as a function of their separation distance. The potential well shows a minimum at the equilibrium distance, where attractive and repulsive forces balance. At short distances, the repulsive force dominates due to Pauli exclusion, while at longer distances, van der Waals attraction prevails.

**1.1 PREVIOUS METHODS**: Before Basin-Hopping was introduced by Wales and Doye (1997), scientists tried several other methods to find the global minima of atomic clusters like Lennard-Jones clusters.[1] Here's a detailed overview:

**1.1.1 Simulated Annealing** (**SA**): Simulated Annealing is an optimization algorithm used for large configurational spaces and used by Wille to find local minima for small cluster sizes[9, 10],

but failed to apply to LJ clusters. Simulated annealing is based on slowly cooling metals to remove defects. It works by randomly changing atomic positions and accepting changes with a probability that gets smaller over time. This method is widely used where many local optima render problems difficult to solve. Compared with other methods like gradient descent that tend to become trapped, Simulated Annealing applies controlled randomness to avoid local minima and probe the solution space more comprehensively. It requires many iterations, and it is a slow convergence method.

**1.1.2: Genetic Algorithm**: The method is inspired by Charles Darwin's theory of natural selection. A genetic algorithm (GA) is a technique that can be applied to determine the optimal solution to a problem by simulating how living organisms evolve naturally. The most successful results for global optimization for LJ clusters are determined by a genetic algorithm.[8, 11]

Studies shown by Deaven et al. utilized GAs to discover the minimum energy configurations for 100-atom clusters,[1] and their solutions equaled known previously to these clusters. They did not find the global minimum for 69-atom clusters, nor sizes 75-78 atoms.

Niesse and Mayne's research discovered the LJ38 truncated octahedron structure, but it was much slower (approximately 25 times slower) to discover this compared to the global minima for other cluster sizes, including those with icosahedral symmetry. This method is good for a large number of atomic clusters, but it is parameter sensitive.

**1.1.3: Hypersurface deformation method**: The Hypersurface Deformation approach seeks to make the optimization process easier by transforming to the potential energy surface (PES).[12] It does this by lowering or smoothing the energy barriers between various local minima, enabling the system to transition more easily among structures. This greatly enhances the capacity to escape deep local traps that could otherwise block global searches. Deformation is generally implemented through the smoothing functions on the native surface.

But this method has severe limitations. Over-smoothing can warp the topology of the PES, in those systems where quantitative energy differences are important, for example, in Lennard-Jones clusters, even minimal warping can result in mistaken conclusions regarding the most stable geometry. Thus, though hypersurface deformation can be an effective exploration tool, it needs to be employed with the utmost care so as not to lose the physical interpretation of the initial energy landscape. Pillardy and Piela did manage to discover the 38-atom truncated octahedron,[13] but other workers were even stuck with simpler problems such as LJ8 and LJ9,[14] having merely 8 and 21 minima on their energy surface.[1]

Despite all this, most of these earlier techniques had limitations when applied to clusters like Lennard-Jones systems, which possess extremely complicated landscapes with deep wells and high barriers. So, applying the Basin-Hopping method, which is the powerful method for global optimization.[1]

## 2: METHODOLOGY

Basin-hopping is an optimization technique used to determine the system's lowest-energy structure by altering the manner in which the potential energy surface (PES) is searched. Rather than acting directly on the original rough landscape of hills and valleys, basin-hopping re-maps PES as a less complicated landscape composed only of local minima.

The concept is simple; the system is perturbed randomly (its atoms are moved a little) and then locally minimized to reach its nearest minimum. After that move is accepted based on energy difference, if the energy difference is negative than the previous move, then it is acceptable and not dependent upon the initial random displacement. In this manner, the algorithm traverses from basin to basin (staircase structure illustrated in Fig. 3) like leaping from valleys rather than getting stuck in rugged parts of the PES.

This change makes escaping local traps considerably simpler and roaming the energy landscape more effectively. Basin-hopping is especially useful because it keeps the physical aspects of the system intact while discovering the real global minimum. That's why it came to be regarded as one of the most effective methods for minimizing Lennard-Jones clusters and other complicated molecular systems.

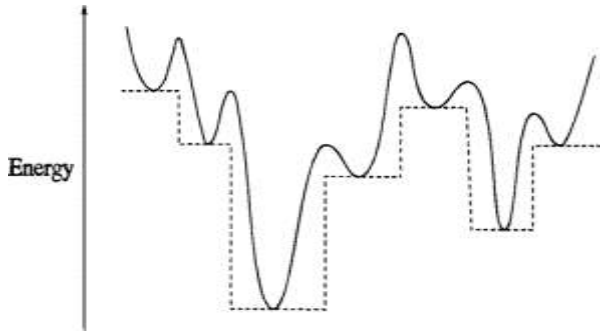



Fig.3: A schematic diagram illustrating the effects of energy transformation for a one-dimensional example. The solid line is the energy of the original surface, and the dashed line is the transformed energy Ẽ.[1]

### 2.1: Basin Hopping Optimization Algorithm with Code Implementation

The global optimization of Lennard-Jones (LJ) clusters using Basin-Hopping uses the following steps:

**Step 1: Initialize Random Atomic Positions**

First, create an initial random configuration of N atoms within a cubic simulation box, then Random coordinates are assigned uniformly within a cube (typically in the range [−2,2] along each axis using NumPy's random number generator. The positions are stored as a single array to

fit the input format required by the optimizer. Which is implemented inside **optimize_lj_cluster()** in optimizer.py file.

**Step 2: Compute Pairwise Lennard-Jones Potential**

Now, find the Total Potential energy of the initial atomic configuration based on the pairwise LJ interaction. Pairwise distances are computed using **`scipy.spatial.distance.pdist()`** and then expanded with squareform() to obtain the full distance matrix. The Lennard-Jones potential is calculated for each atomic pair. Self-interactions are avoided by setting the diagonal elements of the distance matrix to infinity.

The total potential energy is normalized by dividing the pairwise sum by two to avoid double-counting. And this is handled by **`lj_potential()`** function in **`optimizer.py.`**

**Step 3: Local Minimization Using L-BFGS-B (Limited-memory Broyden–Fletcher–Goldfarb–Shanno with Bounds).**

After finding LJ pairwise interactions, relax the initial structure to find a nearby local minimum on the potential energy surface (PES).[15] Local minimization was performed using the L-BFGS-B algorithm[16] as implemented in scipy.optimize.minimize(). The method optimizes the atomic positions to lower the energy, but it does so efficiently by estimating the Hessian matrix, which accelerates the process. After minimizing the structure, it's now ready to be used as the starting point for the subsequent step. The local minimization routine is implemented in the **`local_minimization()`** function within the **`optimizer.py file.`**

**Step 4: Make Random Perturbation (Monte Carlo Move)**

Now that the structure is locally minimized, the next step is to add a small random perturbation to the atomic positions. Because the structure should not be stuck in the same area, that's why add a random perturbation to the atomic positions. control the magnitude of the perturbation with a "step size" (set at 0.5 units), which means that the new structure remains within a sensible range and does not become too distorted. This step generates a "new trial structure." This step is done internally and performed by the **`basinhopping()`** function in **`SciPy.`**

**Step 5: Minimize Energy of the Perturbed Configuration Using L-BFGS-B**

Once the perturbation is added, again use L-BFGS-B to minimize the energy of the perturbed structure.

This is another cycle of local minimization, perturbing the structure to lower the energy to as low as possible in the new structure. This step is managed by passing special minimizer settings (through **`minimizer_kwargs`**) to the **`basinhopping()`** function.

**Step 6: Accept or Reject the New Structure through Metropolis Criterion**

This is the most important step as it Accepts or rejects the new configuration depending on its energy. If the new minimized structure has lower energy than the old one, accept it automatically. But if the energy is higher, still accepts the new configuration with some probability, depending on the Metropolis criterion:

$$P = \exp(-\Delta E/T)$$

ΔE is the difference in energy and T is Temperature (in reduced units T= 1.0) This is handled within **`basinhopping()`**, utilizing a user-defined callback function **`bh_callback()`** to monitor the history of energies and determine which configurations should be accepted.

In short, this entire process is to fine-tune the system's atomic positions, introduce some random modifications to seek new configurations, and then quench the structure down to stable state again.

These iterations are continued for a sizable number of times (e.g., 5000), letting the system roam over various basins and make its way toward the actual global minimum.

Every cycle: **Perturb → Minimize → Accept/Reject → Update Energy Records**

Such repeated search is what enables Basin-Hopping to efficiently sample the PES of atomic clusters.

## 2.2: Code Structure Overview

The project's codebase was structured in a modular way to isolate important functionalities. The driver script is the primary script, which invokes functions from the optimizer.py, visualization.py, and io_utils.py modules. The optimizer.py module is responsible for the core optimization functionality, such as the evaluation of the Lennard-Jones potential, local minimization via the L-BFGS-B algorithm, and the global Basin-Hopping search strategy. The

visualization.py module is used to plot energy evolution plots, plot cluster structures, and animate cluster evolution. The io_utils.py module is used for file I/O operations like saving atomic structures as XYZ files and storing the energy trajectory. The modularity allows for ease of code clarity, maintenance, and extension for future investigations.

# 3: RESULTS AND DISCUSSION

## 3.1: Global minima of LJ clusters

Basin-hopping algorithm has successfully located all the lowest known minima up to N=40, including icosahedral structure (LJ13) and non-icosahedral structure (LJ38), TABLE 1 and Fig. 4a. The total number of searches was constant in these estimates to give a simple reference criterion. Indeed, most of the global minima were identified in over one of the independent Monte Carlo runs. The global minima for the smallest clusters were found within several steps in every one of the four runs.

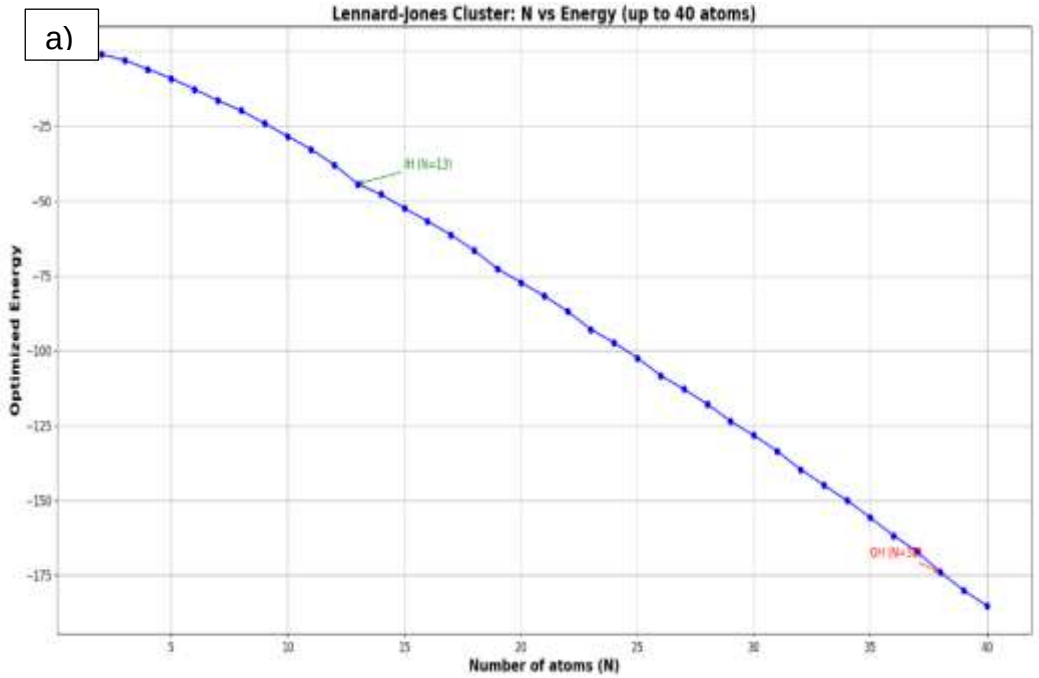
**TABLE 1: GLOBAL MINIMA OF LJ POTENTIAL UP TO N=40**

| N | Optimized energy |
|---|---|
| 2 | -1.000 000 |
| 3 | -3.000 000 |
| 4 | -6.000 000 |
| 5 | -9.103 852 |
| 6 | -12.712 062 |
| 7 | -16.505 384 |
| 8 | -19.821 489 |
| 9 | -24.113 360 |
| 10 | -28.422 532 |
| 11 | -32.765 970 |
| 12 | -37.967 600 |
| 13 | -44.326 801 |
| 14 | -47.845 157 |
| 15 | -52.322 627 |
| 16 | -56.815 742 |
| 17 | -61.317 995 |
| 18 | -66.530 949 |
| 19 | -72.659 782 |
| 20 | -77.177 043 |
| 21 | -81.684 571 |
| 22 | -86.809 782 |
| 23 | -92.844 472 |
| 24 | -97.348 815 |
| 25 | -102.372 663 |
| 26 | -108.315 616 |
| 27 | -112.873 584 |
| 28 | -117.822 402 |
| 29 | -123.587 371 |
| 30 | -128.286 571 |

| | |
|---|---|
| 31 | -133.586 422 |
| 32 | -139.635 524 |
| 33 | -144.842 719 |
| 34 | -150.044 528 |
| 35 | -155.756 643 |
| 36 | -161.825 363 |
| 37 | -167.033 672 |
| 38 | -173.928 427 |
| 39 | -180.033 185 |
| 40 | -185.249 839 |

To confirm the validity of optimization, I created a parity plot of my calculated minimized energies versus the respective reference energies from the Wales database.

As shown in Fig. 4b, all points are perfectly on the parity line (y = x), showcasing complete agreement between our calculations and the reference values. There is no observable deviation or scatter, which verifies that the local minimization and basin-hopping method is correct in reproducing known stable configurations. The straight-line trend for all data points shows that the optimization correctly identified the desired minima without any energy discrepancies.



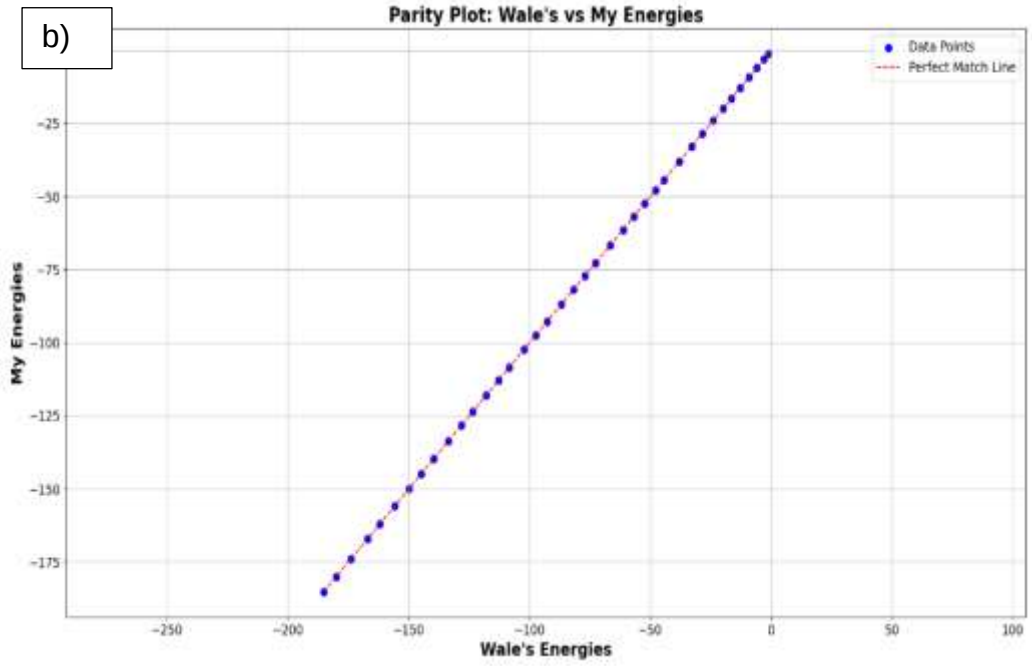



Fig. 4: a) Optimized energy of the clusters (E) as a function of cluster size (N). b) Parity plot showing the optimized energies of David Wale's clusters vs. the optimized energies of my clusters.

### 3.2: Energy evolution for LJ38 cluster:

Fig. 5. To monitor the stability of the LJ38 cluster as a function of optimization, a plot of energy evolution versus number of basin-hopping steps. The staircase line clearly shows what happens to the system as it explores lower-energy configurations. Starting, the system has an initially high-energy, unstable form large drops in energy are seen in the early steps. This is because the local minimization is quickly refining the structure, exploring more stable neighboring minima. When more steps are taken, energy fluctuations are reduced, and the system begins to stabilize in deeper minima. In order to escape the shallowness of local minima, towards the later steps, energy becomes constant and fluctuations are negligible, indicating that the system has achieved a highly stable (presumably global) minimum**.** From the graph, we can see that in nearly 310 steps, it achieves a global minimum.

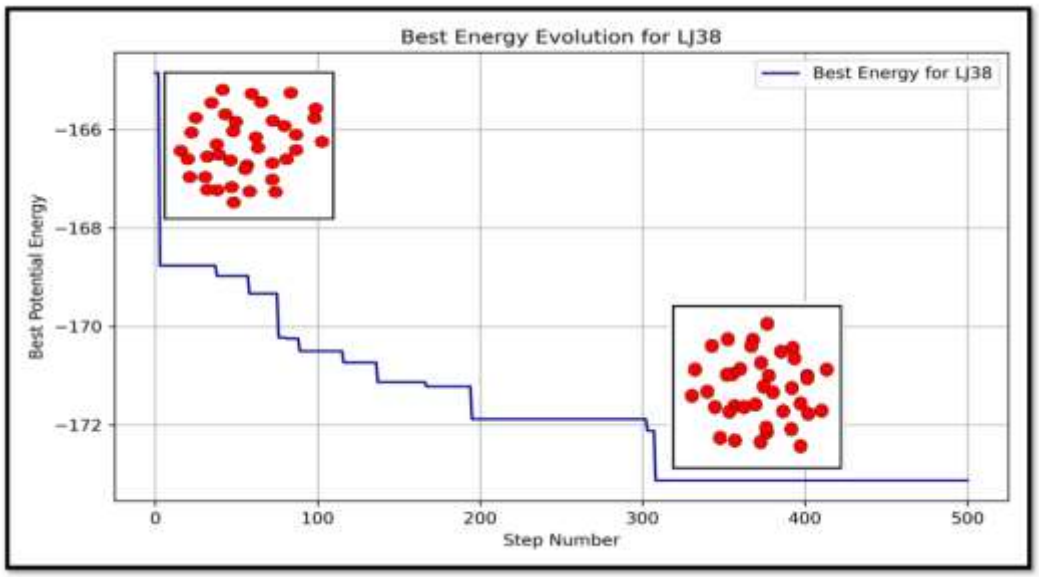



Fig. 5: Energy evolution of the LJ38 cluster during basin-hopping optimization. The initial structure undergoes significant energy reduction in the early stages, with gradual stabilization toward a deep minimum as the number of steps increases.

The following are the optimized structures, demonstrating their configurations after energy minimization:

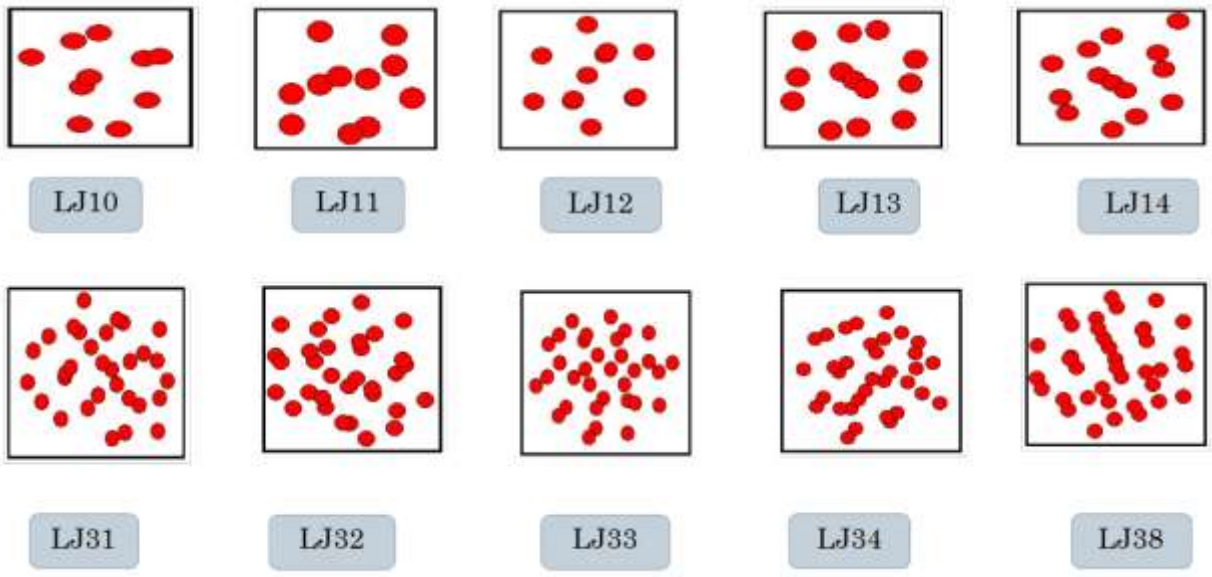



Fig .6: Optimized structures of the clusters after energy minimization, showcasing the final stable configurations

### 3.3: Potential energy vs No. Of steps

To study how the potential energy changes with optimization for various clusters (LJ11, LJ26, etc.), I plotted Potential Energy vs. Number of Steps for every cluster, Fig. 7. These plots show the process of energy minimization through different basin-hopping steps and how the system becomes stable over time. There are some common trends observed in all clusters (LJ11, LJ26, etc.), like every cluster begins with a comparatively high potential energy because the starting atomic positions are away from the global minimum.

In the first basin-hopping steps, there are large drops in potential energy. It means that the system is improving the configuration quickly by searching around minima. At later stages of the optimization, the drops in energy are smaller, and the low-energy structures are accepted. These transitions are permitted by the Metropolis criterion and give local minima.

After several steps, the potential energy converges to a stable value, which indicates that the system has converged to a more stable state. The energy oscillation is minimal, reflecting convergence to a local or global minimum.

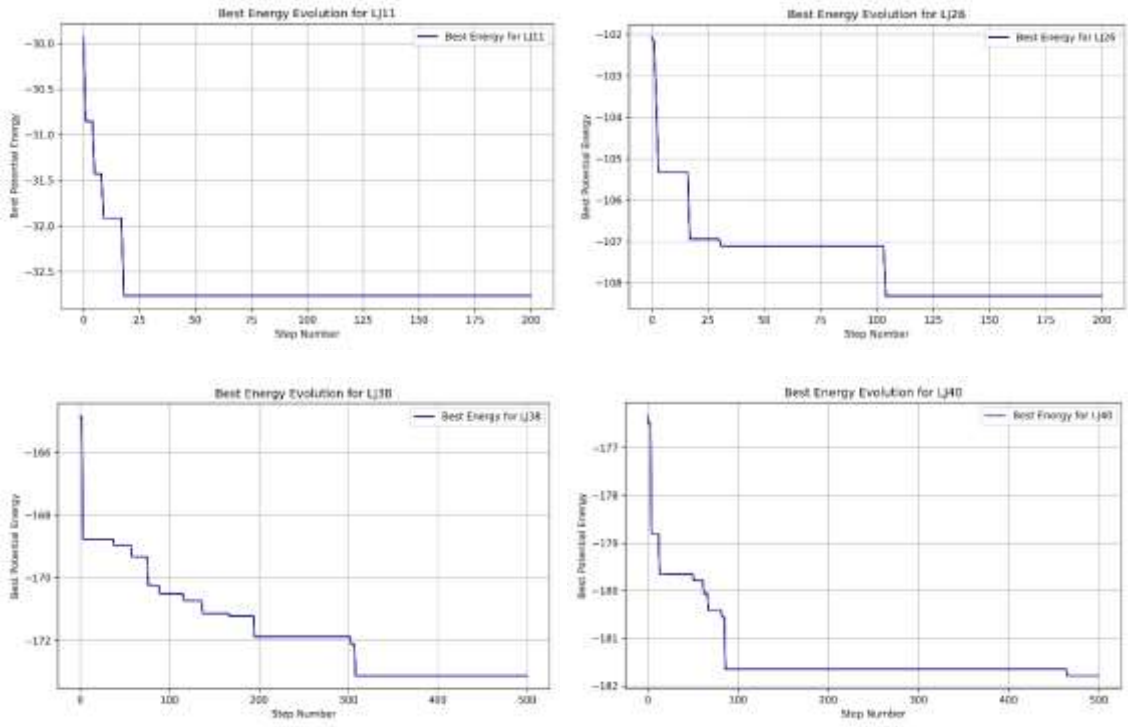



Fig 7: Potential energy evolution for various LJ clusters (LJ11, LJ26, etc.) as a function of basin-hopping steps.

## 4: CONCLUSION

In this work, the Basin-Hopping method was successfully utilized to perform global optimization of Lennard-Jones (LJ) atomic clusters. With the combination of random perturbations and local minimization with the L-BFGS-B algorithm,

The system effectively explored the potential energy surface and accurately found low-energy structures, correctly identifying known global minima, e.g., the truncated octahedron structure of the $LJ_{38}$ cluster.

The modular structure of the Python code, with separate optimization, visualization, and input/output modules, allowed for greater flexibility, transparency, and ease of extension. Real-time energy monitoring during optimization provided valuable insights into convergence behavior.

Results confirmed that Basin-Hopping is an effective algorithm for rugged PES and local minima multi-global optimization problems. Developed herein, this algorithm is conveniently expandable into large clusters and other systems beyond atomic clusters as well, furnishing a groundwork firm enough to form the core for further explorations in this field, such as in nanomaterials, catalysis, or biological molecules.

This study not only confirmed existing scientific norms but also provided the groundwork for a strong and flexible computational framework that will be able to solve more sophisticated global optimization problems in the future.

## 5: ACKNOWLEDGMENTS

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