# Basin hopping method for global optimization of Lennard Jones clusters

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**ABSTRACT:** Basin hopping is a random algorithm which attempts to find the global minimum of a scalar function of one or more variables. Using this global optimization technique and various parameters in our programming for number of iterations, temperature, and step-size, we seek to determine ground states for Lennard Jones clusters for 13, 14, and 15 atom systems. Values are then compared to experimental values found within The Cambridge Cluster Database.

# 1. INTRODUCTION

## 1.1 Theoretical Background

Characterization of complex systems often poses very hard global optimization problems with many variables. Algorithms that target such problems largely build on or combine four main approaches: deterministic, stochastic, heuristic, and smoothing. All these algorithms are challenged by systems where the variable space contains multiple, distinct minima. While most algorithms can efficiently find a minimum, not all can feasibly locate the global minimum.[1]

Basin hopping (BH) is a global optimization framework that is particularly suited for multivariable, multimodal optimization problems. It is an optomization technique in which the potential energy surface is transformed into a collection of interpenetrating staircases.[2] Each step can be construed to be a well representative of a local minimum, such that "hopping" to each local minimum on a topological representation of energy can lead to finding the global minimum of the system. In other words, BH combines heuristic procedures with local searches to enhance its exploration of the given variable space, conducted as a series of perturbations followed by local optimization.

For our experiment, we will be using a simple system that can be represented by the Lennard-Jones potential. It describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation, shown in Figure 1.1. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces. It is represented as follows,

$$V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad [1.1]$$

where V is the intermolecular potential between atoms or molecules, ε is the well depth and a measure of how strongly the particles attract to each other, σ is the distance at which the intermolecular potential between the two particles is zero, and r is the separation between particles (measured from the center of one particle to the center of the other particle). For our calculation, we will be using reduced units such that σ=ε=1.

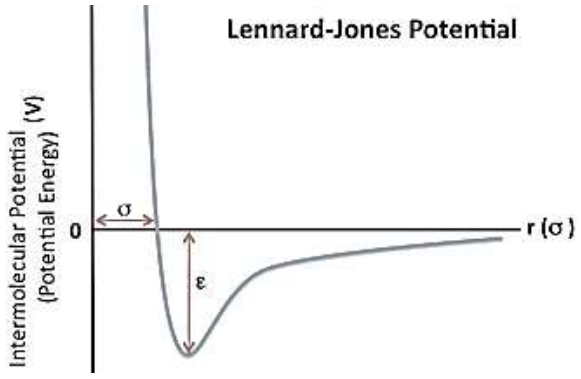



**Figure 1.1**. A plot of the Lennard Jones potential, displaying potential energy vs separation between particles.

## 1.2 Methods

To determine ground states, we will be utilizing Python programming and the SciPy libary. To find the global minimum of a function using a basin-hopping algorithm, we begin by defining our Lennard Jones potential function, Eq. [1.1], as

```
def LJ(r):
    r6 = r**6
    r12 = r6*r6
    return 4*(1/r12 - 1/r6)
```

We then calculate the total energy input in terms of positions of a three-N array and an initial position, which represent the atomic positions and ultimately the total energy. For this procedure, we use the numpy library.

```
import numpy as np

def LJ(r):
    r6 = r**6
    r12 = r6*r6
    return 4*(1/r12 - 1/r6)

def total_energy(positions):
    E = 0
    N_atom = int(len(positions)/3)
    for i in range(N_atom-1):
        for j in range(i+1, N_atom):
            pos1 = positions[i*3:(i+1)*3]
            pos2 = positions[j*3:(j+1)*3]
            dist = np.linalg.norm(pos1-pos2)
            E += LJ(dist)
    return E

def init_pos(N, L=5):
    return L*np.random.random_sample((N*3,))
```

To perform the task of basin hopping, we utilize optimization within SciPy and adjust the parameters *niter*, *T*, and *stepsize*, or the number of basin hopping iterations, the "temperature" parameter for the accept or reject criterion, and the initial step size for use in the random displacement, respectively. The code necessary to implement basin hopping via SciPy, without defined parameters, can be represented as

```
from scipy.optimize import basinhopping

N_atom =
pos = init_pos(N_atom)
res = basinhopping(total_energy, pos, niter= , T= , stepsize= , disp=True)
```

To find the parameters which could lead to the global minimum otherwise known as the ground state, multiple tests are performed while varying the parameters of basin hopping. During this process, it is understood that higher temperatures mean that larger jumps in function value will be accepted. For best results the T parameter should be comparable to the separation, in function value, between local minima.

# 2. EXPERIMENT & RESULTS

## 2.1

Through various parameter configurations, it was concluded

that the energy calculations were stable when the number of basin hopping iterations was 20 and the initial step size for use in the random displacement was set to 3.0. Setting these two parameters, temperature was varied and it was concluded that consistent global minimum energy values were calculated between specific temparature values; increasing with the number of atoms.

For 13 atoms, two of numerous stable configurations for parameter settings are as follows

niter = 20, T = 0.5, stepsize = 3.0
niter = 20, T = 1.0, stepsize = 3.0

Each of these basin hopping operations are represented in Figure 2.1, which provide visual representations of local and global minimums of energy values of -44.3268 eV.

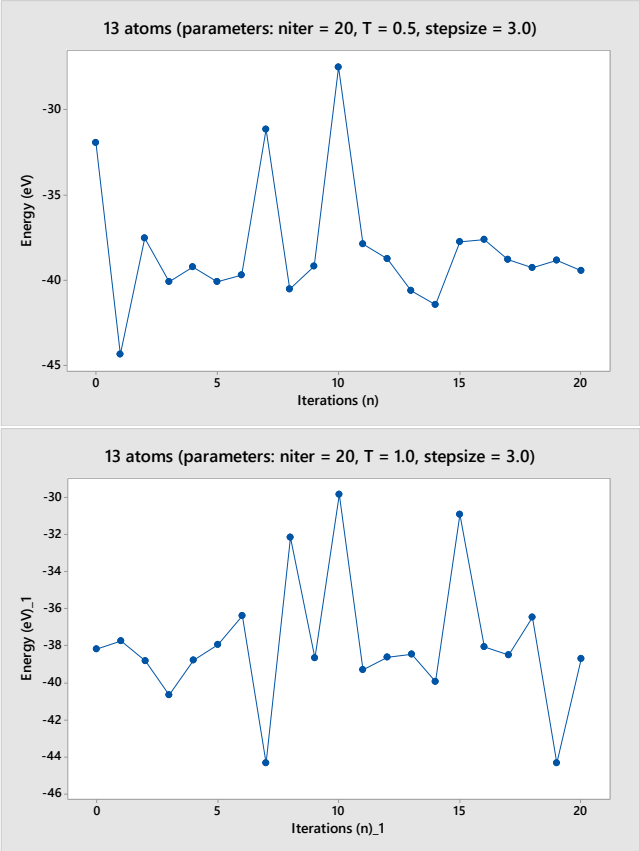



**Figure 2.1.** Basin hopping plots for 13 atoms, each with a varied T parameter, both showing global minimum values of -44.3268 eV.

For 14 atoms, two of numerous stable configurations for parameter settings are as follows

niter = 20, T = 2.7, stepsize = 3.0
niter = 20, T = 2.5, stepsize = 3.0

Basin hopping operations for 14 atoms are represented in Figure 2.2, which provide visual representations of local and global minimums of energy values of -47.8452 eV

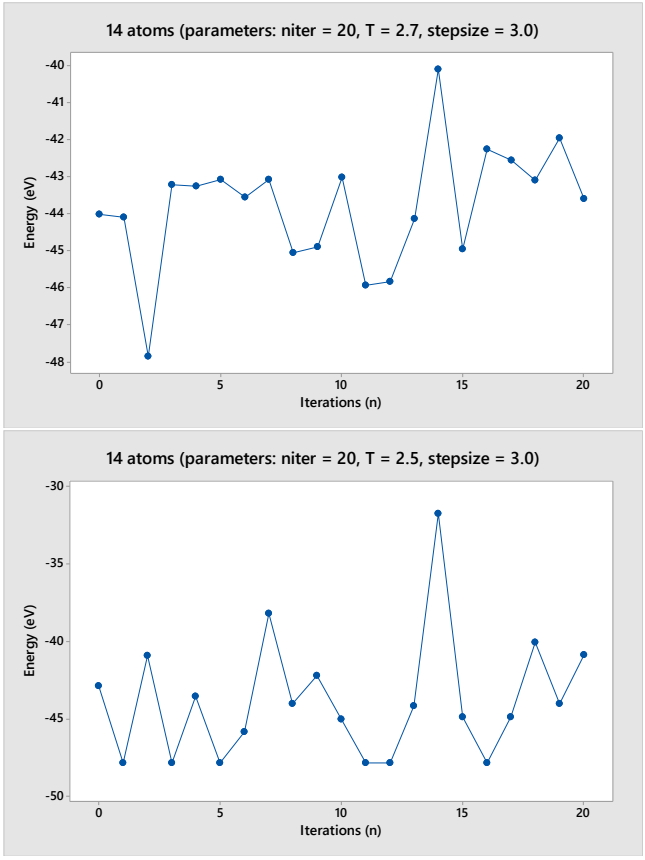



**Figure 2.2.** Basin hopping plots for 14 atoms, each with a varied T parameter, both showing global minimum values of -47.8452 eV.

For 15 atoms, two of numerous stable configurations for parameter settings are as follows

niter = 20, T = 3.5, stepsize = 3.0
niter = 20, T = 3.7, stepsize = 3.0

Basin hopping operations for 15 atoms are represented in Figure 2.3, which provide visual representations of local and global minimums of energy values of -52.3226 eV.

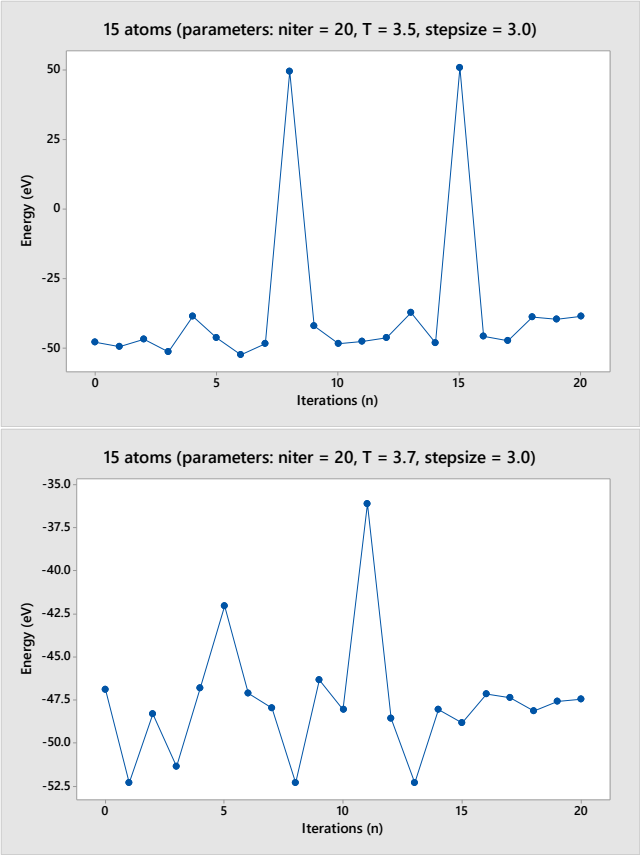



**Figure 2.3.** Basin hopping plots for 15 atoms, each with a varied T parameter, both showing global minimum values of -52.3226 eV.

After using the basin hopping algorithm to determine global minimums for systems of 13, 14, and 15 atoms, the values are then compared with experimental values provided via the Cambridge Cluster Database, as represented in Table 2.1. The comparison of data suggests that the basin hopping method and parameters used during this experiment was sufficient in determining global minimum values that match the Cambridge Cluster Database.

| Atoms | Basin Hopping Calculation | Cambridge Cluster Database |
|---|---|---|
| 13 | -44.3268 | -44.326801 |
| 14 | -47.8452 | -47.845157 |
| 15 | -52.3226 | -52.322627 |

**Table 2.1.** A comparison of our values with those determined by D. J. Wales and his group, which are found in the Cambridge Cluster Database

## 2.2 Methods of Further Investigation

To seek additional relationships in the basin hopping calculations that determine potential values for our 13, 14, and 15 atom systems, the varying temperature parameter was reviewed. Among the sample of systems (13 atoms, 14 atoms, 15 atoms), it was noticed that stability of the numerical calculations had a relationship with the number of atoms in each system and temperature. As shown in Figure 2.4, a linear relationship was found between atoms and temperature, with accurate intermolecular potentials (with respect to those in the Cambridge Cluster Database) being found for systems with increasing atom size as the temperature parameter is inceased. To determine if causation exists within this observation, many additional numerical tests and parameter variations would be necessary, which is a bit too robust for our project; however, the discovered trend is intriguing and can be explored in a separate project.

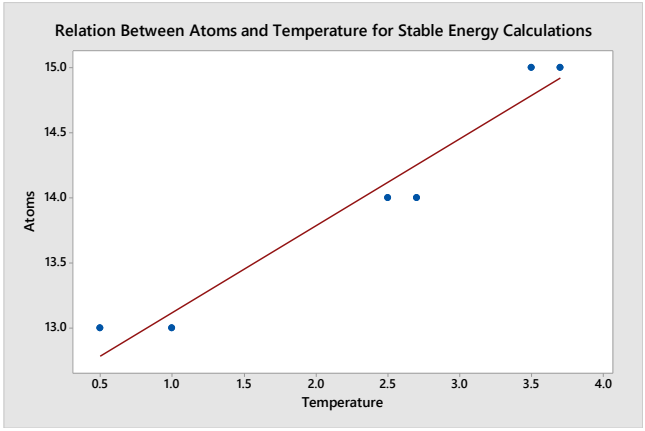



**Figure 2.4.** A simple regression plot showing the relationship between atoms and temperature.

To obtain additional insight into optimization and exploration on energy landscapes, basin hopping can be accompanied by disconnectivity graphs, which provide a visualization of the energy of the system. Using pele, a python partial-rewriting of GMIN, OPTIM, and PATHSAMPLE: fortran programs written by David Wales of Cambridge University and collaborators, disconnectivity graphs can be rendered.

Due to operating system restrictions and the nature of the code involved, we have simply provided a demonstration of the use of pele via python for a system of 16 atoms in an effort to suggest a method of deeper investigation into multi-atom systems. The example shows how to use double-ended-connect to connect the minima in an existing database.

First, an example system of the Lennard-Jones cluster with a small number of atoms is used. Since there is no database for the example, one is built using basinhopping.

```
from pele.systems import LJCluster
from pele.utils.disconnectivity_graph import DisconnectivityGraph, database2graph

natoms = 16
system = LJCluster(natoms)
```

A database is created, where the minima and transition states will be stored.

```
db = system.create_database()
```

Basin hopping is used to build a database of minima.

```
bh = system.get_basinhopping(database=db, outstream=None)
bh.run(100)
```

The logging module is then used to enable printing for connect runs.

```
import logging
logger = logging.getLogger("pele.connect")
logger.setLevel("WARNING")
```

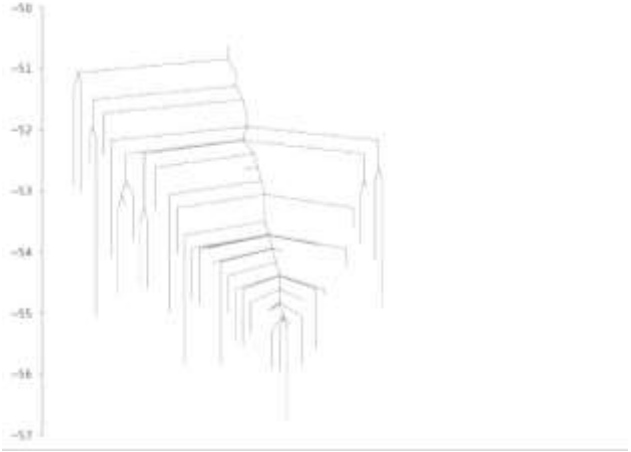
Perform multiple double ended connect runs to find transition states connecting the minima.

```
from pele.landscape import ConnectManager
manager = ConnectManager(db)
for i in xrange(20):
    min1, min2 = manager.get_connect_job()
    connect = system.get_double_ended_connect(min1, min2, db, verbosity=-1)
    connect.connect()
```

Now that there is a database with minima and transition states, the disconnectivity graph can be constructed.

```
print "number of minima", db.number_of_minima()
print "number of transition states", db.number_of_transition_states()

graph = database2graph(db)
dgraph = DisconnectivityGraph(graph)
dgraph.calculate()
dgraph.plot()
import matplotlib.pyplot as plt
plt.show()
```




## 3. CONCLUSION

We have shown that the method of basin hopping and parameter variations implemented in this experiment yield intermolecular potential values for systems of 13, 14, and 15 atoms, that equal the energy values presented in the Cambridge Cluster Database. Using the programming code provided in section 1.2, we determined that for the three atoms selected, there is a correllation between atom size and temperature that provides for increased accuracy in finding experimentally-known values for energy. For 13 atoms, 14 atoms, and 15 atoms, we found global minimums to be -44.3268 eV, -47.8452 eV, and -52.3226 eV, respectively. Additional observations were made during the experiment, that may provide further insight into the nature of the programming and operations, that pertain to relationships between parameters and energy landscapes via disconnectivity graphs.

## REFERENCES

[1]Wales, D., & Doye, J. (1997). *Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms*. JPC, 101, 5111 – 5116.

[2]Olson, B., Hashmi, I., Molloy, K., & Shehu, A., (2012). *Basin Hopping as a General and Versatile Optimization Framework for the Characterization of Biological Macromolecules*. AAI, 2012, 19 pages.

[3]Wales, D. J., Doye, J. P. K., Dullweber, A., Hodges, M. P., Naumkin, F. Y., Calvo, F., Hernandez-Rojas, J., & Middleton, T. F. (1997). The Cambridge Cluster Database, http://www-wales.ch.cam.ac.uk/CCD.html.