An Investigation Of The Lennard-Jones Clusters Using The Basin Hopping Global Optimization Technique

Blake Harris

November 30, 2017

1 Abstract

Basin-hopping is a stochastic global optimization technique used to find global minima of a function. Using this technique, experiments were run to find the ground states for 3 different Lennard-Jones clusters. Code was written using Python 3 to carry out this task, and the results for 10,15, and 20 atom systems were compared to the Cambridge cluster database values database.

2 Introduction

While the reason may vary, it is often useful to find local minima or maxima. This is often covered using various optimization techniques. In many cases, what is desired is the global minima or maxima. This is where a subset of these techniques known as global optimization techniques become an invaluable tool. Global optimization techniques have been important method in the analysis of complex systems.

One such technique is known as basin-hopping. It a stochastic optimization method that uses random variables over many iterations to find the global extrema. The basin-hopping technique transforms the potential function into a series of steps that have the same value as the local minima.

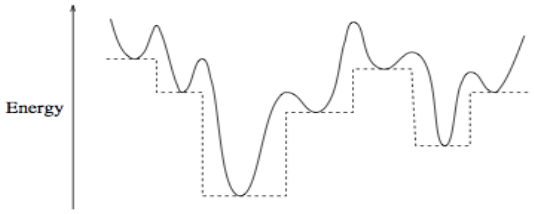

Figure 1: A curve with the overlayed steps used in the basin-hopping technique.

These steps are iterated over using the following three step process. 1. Initial random selection of coordinates. 2. Reading of the local minimum. 3. The local minimum is either accepted or rejected using various methods. That is, a random coordinate on the function is selected. then, over each iteration, the random coordinate has a chance to "hop" into a new local minimum. The value of the local minimum is then compared to the previous values. The one used in SciPy, and developed by the Wales group, uses the Metropolis criterion of the standard Monte Carlo algorithms as its acceptance and rejection process.

Lennard-Jones clusters have been used as common test systems for global optimization algorithms such as this one. The Lennard-Jones clusters are models that approximates interactions for neutral atoms or molecules, and helps to predict the propensity for a number of atoms, N, to become geometrically arranged. The potential energy of the interaction is shown below,

$$V = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] \qquad (1)$$

where ε n is the potential well depth, σ is the distance where inter-particle potential is zero, and r is the distance between the particles. It is interesting to note that genetic algorithms and basin-hopping are the only unbiased global optimization techniques that have successfully found a decahedral global minima.

3 Methods

Python 3 along the built-in basin-hopping optimization algorithm from the SciPy library were used to conduct this study. The Lennard-Jones clusters was used to investigate the properties of the basin-hopping algorithm. A code was set up to find the ground states for Lennard-Jones Clusters for three different numbers of atoms. To do this the Lennard-Jones potential function was defined in the code using features from the NumPy library.

```
import numpy as np

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

The total energy was then defined using arrays and the initial atomic positions.

```
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,))
```

The basin-hopping algorithm was imported from the scipy.optimize package, and the basinhopping statement was included in the code.

```
import numpy as np
from scipy.optimize import basinhopping


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,))


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

The parameters of the basin-hopping algorithm were then specified and the code was run. Each of the varied parameters has a specific function. The niter= dictates the number of iterations of the three-step cycle. T, or temperature, controls the accepted size of a jump in the function value. And finally the step size controls the x-axis movement of the test point. The results were compared to the Cambridge cluster database values to determine the effect of the parameters. These parameters were then varied, and the ground state given by the algorithm was again compared to the database values.

4 Results and Discussion

Three numbers, 10, 15, and 20, were selected to be the number of atoms for these tests. The initial parameters used were random and are shown below.

niter	T	stepsize
30	1.5	3.0

The criterion used for the optimal parameter selection were as follows: 1: The Lennard-Jones cluster value given by the basin-hopping algorithm matched the Cambridge cluster database value. 2: The value was obtained in constantly. 3: The value was obtained in a finite, and reasonable amount of time. A table of the Cambridge cluster database values for 10, 15, and 20 atoms is shown below.

N = 10	N = 15	N=20
-28.422532	-52.322627	-77.177043

The test were trial and error in nature. All parameters were varied multiple times and in different combinations until a combination was found that yielded the correct energy. For the 10 atom system, it was found that niter=20, T=1, and step size=3.0 yielded the Cambridge cluster database value consistently. The found global minimum had a value of -28.4225. This trial was the easiest of the three to run, as the global minimum was found in under 10 iterations. A graph of energy vs steps is shown below.

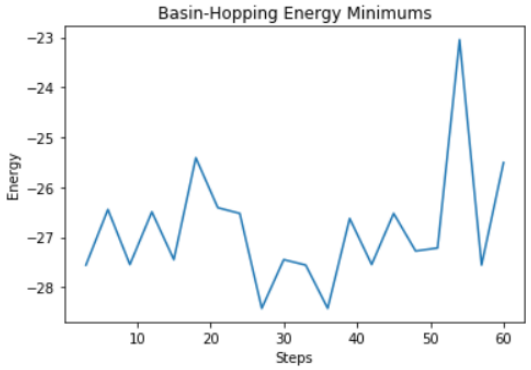

Figure 2: This graph shows that the global minima was found twice in 20 iterations.

The 15 atom system was more complicated and required more time. The number of iterations had to be increased before the correct energy was seen. In the first attempt with 30 iterations, the correct energy was found on the 4th step and had a value of -52.3226. A graph showing this is shown below.

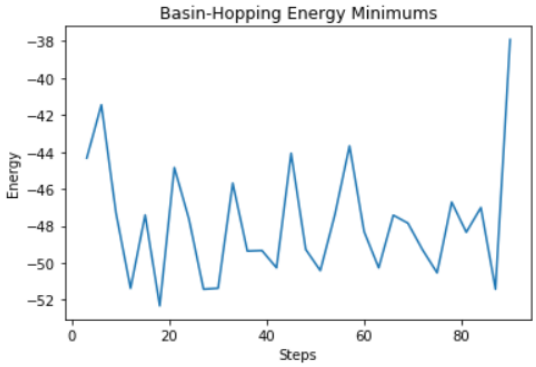

Figure 3: This time, the global minima was found only once.

The 20 atom system, gave me the most trouble. In the end, the value given by the Cambridge cluster was never reached. Many trials were done and all failed. The minimum that was found varied wildly, but the lowest was -74.6152. The number of iterations was increased to 50 and both the temperature and step size were varied extensively. The last trials were done in 0.1 increments for both. There are many variables at play here and it is currently unknown which one, or combination of them caused the failure. A graph showing the results for the 50 iterations, T=3.7, and stepsize =2.5 trial is shown below.

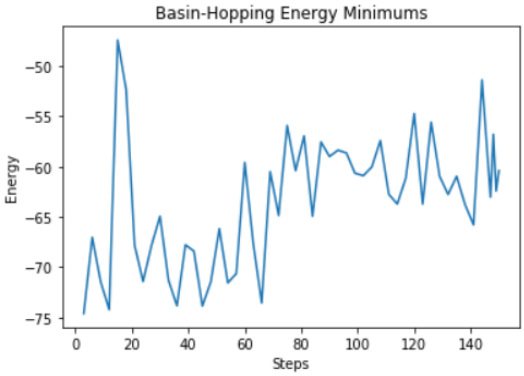

Figure 4: This graph seems to have a increasing trend in the energy. It is currently unknown why.

Throughout the experiment trends two trends became clear. As the number of atoms in the system increase, the number of iterations and temperature needed to increase as well. The exact relationship was undetermined during this experiment, but it might be worth further investigation.

5 Conclusion

An experiment was performed to find the ground states of 3 different Lennard-Jones clusters. The 3 experiments consisted of 10, 15, and 20 atoms systems which were subjected the basin-hopping global optimization technique to find their respective

ground states. The number of iterations, temperature, and stepsize were all varied to find the most optimal conditions for the optimization of each system. The values obtained were checked against the Cambridge cluster database, and it was found that two out of the three experiments were a success. A broad trend was noticed, in that as the number of atoms increases, generally the step size and temperature will need to increase as well. Further investigation into the exact nature of this trend is considered for the future.

6 References

Wales, D J, and Doye J P K, Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters Containing up to 110 Atoms. Journal of Physical Chemistry A, 1997, 101, 5111.

Wales Group.Table of Lennard-Jones Clusters Minimum Values. http://doye.chem.ox.ac.uk/jon/structures/LJ/tables.150.html