



DEPARTMENT OF PHYSICS

# GLOBAL OPTIMIZATION IN COMPLEX SYSTEMS

*Final Degree Project*

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# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Summary in Spanish . . . . .	2
<b>2</b>	<b>Lennard-Jones potential</b>	<b>2</b>
2.1	Born-Oppenheimer approximation . . . . .	2
2.2	Inter-atomic interaction . . . . .	4
2.3	Description of Lennard-Jones potential . . . . .	4
2.4	Summary in Spanish . . . . .	5
<b>3</b>	<b>Global Optimization Methods</b>	<b>6</b>
3.1	Simulated Annealing (SA) . . . . .	6
3.2	Genetic Algorithm (GA) . . . . .	6
3.3	Basin-Hopping Algorithm (BH) . . . . .	7
3.4	Summary in Spanish . . . . .	8
<b>4</b>	<b>Basin-hopping algorithm</b>	<b>8</b>
4.1	Method followed . . . . .	8
4.2	Energies obtained . . . . .	9
4.3	Summary in Spanish . . . . .	10
<b>5</b>	<b>Results and discussions</b>	<b>10</b>
5.1	Stability . . . . .	11
5.2	Icosahedral structures . . . . .	11
5.3	Nonicosahedral structures . . . . .	13
5.4	Summary in Spanish . . . . .	13
<b>6</b>	<b>Conclusion</b>	<b>14</b>
6.1	Summary in Spanish . . . . .	15
<b>A</b>	<b>Icosahedral structures</b>	<b>18</b>

## List of Figures

1	Representation of LJ potential in a two-particle system. Reduced units used ( $\epsilon = \sigma = 1$ ) . . . . .	5
2	Energy per particle. Red dots correspond to complete Mackay icosahedra. . . . .	10
3	Regular convex icosahedra . . . . .	11
4	Second-order energy difference for up to 55 particles. Red dots correspond to complete Mackay icosahedra. Rest of the dots correspond to especially stable clusters. . . . .	12
5	Mackay and anti-Mackay cubic close-packing schemes.[4] . . . . .	13
6	Geometry given by the global minimum for $N = 13$ . Image represented by the program Avogadro. [8] . . . . .	13
7	Geometry given by the global minimum for $N = 55$ . Image represented by the program Avogadro. [8] . . . . .	14
8	Geometry given by the global minimum for $N = 38$ . Image represented by the program Avogadro. [8] . . . . .	14
9	Geometry given by the second lowest minimum for $N = 38$ . Image represented by the program Avogadro. [8] . . . . .	15
10	Geometry given by the global minimum for $N = 19$ . Image represented by the program Avogadro. [8] . . . . .	18
11	Geometry given by the global minimum for $N = 23$ . Image represented by the program Avogadro. [8] . . . . .	18
12	Geometry given by the global minimum for $N = 26$ . Image represented by the program Avogadro. [8] . . . . .	19
13	Geometry given by the global minimum for $N = 46$ . Image represented by the program Avogadro. [8] . . . . .	19
14	Geometry given by the global minimum for $N = 49$ . Image represented by the program Avogadro. [8] . . . . .	19

# 1 Introduction

Global optimization is a field of great interest in many different branches of science. The objective of global optimization is to find the best global solution of (possibly non-linear) models, in the presence (possible or known) of multiple local minima. Some examples can be seen in advanced engineering design, biotechnology, data analysis, environmental management, financial planning, process control, risk management, scientific modeling, and others. However, this work is going to focus on the optimization of a cluster composed by rare gases atoms.

Following different authors [1][2], one of the simplest models that exhibits such behavior that one may consider is the problem of finding the ground-state structure of a cluster of atoms interacting through a classical Lennard-Jones (LJ) pair potential, given by:

$$V_{LJ} = 4\epsilon \sum_{i < j} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where  $r_{ij}$  is the distance between the  $i$ -th and  $j$ -th particle,  $\epsilon$  and  $2^{1/6}\sigma$  are the pair equilibrium well depth and separation, respectively. In a cluster composed by  $N$  atoms, each pair interacting by a potential of the form (1) will rise to the potential energy surface (PES). One may pose the question "Why is it important to locate the global minimum?" as Roy L. Jhonston stated: "Clusters corresponding to global minima (or low-lying local minima) are the most likely candidates for the most probable structure formed in cluster experiment" [3]. As the number of minima rises exponentially with increasing cluster size [2], finding the global minimum can be very difficult. In Section 4, we will see the LJ potential in more detail.

Studies have shown that the predominant structure from  $LJ_{10}$  to  $LJ_{150}$  are based on an icosahedron packing [1]. However, there are exceptions where the structure formed is nonicosahedral like  $LJ_{38}$ ,  $LJ_{75-77}$  and  $LJ_{102-104}$ . These structures are much more difficult to find than the rest and are a good method to see if the optimization technique used is useful or not. Two requirements that an optimization method must meet are the ability to optimize  $LJ_{38}$  and  $LJ_{75}$ . In Section 5, we will discuss both icosahedral and nonicosahedral structures.

A wide range of studies have tried to answer this problem. Among them, the simulated annealing (SA) which is based on creating a random walk over the PES where moves are accepted by a Boltzmann probabilities. Typically, one starts the SA on sufficiently high temperatures performs several iterations at a fixed temperature and then decreases that temperature logarithmically. As the temperature drops the system becomes trapped in quenches which correspond with low-lying minima or global minimum.

On the other hand, genetic algorithms (GA) use operators based on evolutionary processes such as mating or natural selection. These algorithms are the most efficient and fastest for global optimization [2]. This method will be discussed in greater depth later.

The method used in the present work is the basin-hopping (BH) algorithm which is the first to find the global minimum for  $LJ_{75}$  with an unbiased search [1]. This method is similar to the SA method, it also uses a Boltzmann probabilities to chose between two different energies but it works with fixed temperature. The three methods will be discussed in greater depth in Section 3 and the BH algorithm in Section 4.

Finally, global optimization methods are not just about finding the global minimum, it also gives us a notion about phase transitions or if the potential is physically reasonable [1].

## 1.1 Summary in Spanish

La optimización global de sistemas complejos es un campo de gran interés en distintas ramas de la ciencia. El objetivo de la optimización global es encontrar el mínimo global de energía de un sistema, en la mayoría de los casos basado en un modelo no lineal, en presencia de muchos mínimos locales. Esto es útil en campos como la economía, ciencias naturales o ingeniería. En este trabajo trabajaremos con agregados de gases nobles para encontrar la estructura más probable a bajas temperaturas.

Para ello, usaremos un modelo de interacción entre los átomos basado en el potencial de Lennard-Jones. La interacción entre todos los átomos dará lugar a una superficie de energía potencial cuyo mínimo global está íntimamente ligado con la estructura más probable que formará el agregado.

Por otro lado, presentaremos los tres métodos más usados para resolver este tipo de problemas, mostrando sus puntos fuertes y sus inconvenientes. Estos algoritmos son: algoritmo genético (GA), enfriamiento simulado (SA) y el algoritmo de basin-hopping (BH). Este trabajo se centrará en éste último, el BH.

Por último, presentaremos los resultados obtenidos y discutiremos la utilidad del trabajo, además de proponer algunas mejoras para futura continuación del proyecto.

## 2 Lennard-Jones potential

First of all, we must choose a potential that matches the experimental data. The Lennard-Jones potential is a mathematical model for a pair of neutral atoms or molecules. But first we must ensure that the electronic potential does not affect the results shown. This is possible thanks to the Born-Oppenheimer approximation. Furthermore, we must consider whether there are external potentials or how a third particle affects the potential between two of them. All of these approaches are necessary to simplify the model.

### 2.1 Born-Oppenheimer approximation

The Born-Oppenheimer approximation is an essential element in finding the potential energy surface. It also gives us an example of how different coordinates

can be treated independently. The approximation involves neglect of terms that couple together the electronic and nuclear degrees of freedom. [4]

The Schrödinger's equation for a molecule with  $n$  electrons, mass  $m_e$  and  $N$  nuclei with masses  $M_t$  is

$$\left[-\sum_{t=1}^N \frac{\hbar^2}{2M_t} \nabla_t^2 - \sum_{i=1}^n \frac{\hbar^2}{2m_e} \nabla_i^2 + V(x, X)\right] \Psi(x, X) = E_{TOTAL} \Psi(x, X), \quad (2)$$

where  $x$  and  $X$  are the vectorial positions of the electrons and nuclei respectively.

The potential energy  $V(x, X)$  is given by:

$$V(x, X) = \frac{e^2}{4\pi\epsilon_0} \left[-\sum_{i,t} \frac{Z_t}{r_{it}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{t<s} \frac{Z_t Z_s}{r_{ts}}\right], \quad (3)$$

where  $Z_t$  is the atomic number of nucleus  $t$ ,  $e$  is the charge of the proton.  $r_{it} = |x_i - X_t|$  where  $x_i$  is the vector position of the electron  $i$  and  $X_t$ , the vector position of the nucleus  $t$ . Thus, the first term gives us the electron-nucleus interaction. In the same way we can calculate the electron-electron and nucleus-nucleus interaction. The summatories of the last two terms of the potential have this form so as not to take into account the same potentials twice. Furthermore, Born and Oppenheimer took into account that the mass of the proton is approximately 1836 times greater than that of the electron, and therefore, their reasoning was that the density of the electron would adjust almost instantaneously to the positions of the nuclei. From the classical point of view, electrons are expected to move much faster than nuclei. That will allow us to get rid of the electron-nucleus interaction. Hence, they brought an approximation of the wavefunction that is given by:

$$\Psi(x, X) = \Psi_e(x; X) \Psi_n(X), \quad (4)$$

where  $\Psi_e(x; X)$  is a solution of the electronic Hamiltonian:

$$[\hat{H} - \hat{T}_n] \Psi_e(x; X) = V_e(X) \Psi_e(x; X), \quad (5)$$

$\hat{H}$  is the total Hamiltonian operator, and  $\hat{T}_n$  is the nuclear kinetic energy operator (first term of equation (2)). Thus, we write  $\Psi_e(x, X)$  and  $V_e(X)$  to show that different electronic wavefunctions and energies are obtained for different nuclear configurations.

The potential energy surface defines the variation of the electronic energy,  $V_e(X)$ , with the nuclear geometry [4]. We must know that different solutions of (4) will rise to different PES, so we are going to solve the system for the ground state electronic configurations, which is the most probable solution at low temperatures.

Finally, the appropriate Schrödinger equation for the nuclear wavefunction,  $\Psi_n(X)$ , is

$$[\hat{T}_n + V_e(X)]\Psi_n(X) = E_{TOTAL}\Psi_n(X). \quad (6)$$

## 2.2 Inter-atomic interaction

In general, the way we have to express an inter-atomic potential is

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i^N U_1(\vec{r}_i) + \sum_i^N \sum_{j<i}^N U_2(\vec{r}_i, \vec{r}_j) + \sum_i^N \sum_{j<i}^N \sum_{k<j}^N U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots, \quad (7)$$

where  $U_1$  is the external potential that affects the  $i$ -th particle.  $U_2$  is the potential existing between two particles. We impose the condition  $j < i$  to not count the same interaction twice. Lastly,  $U_3$  is the potential referred to a third particle that affects the pair potential. In general,  $U_3$  and therefore the successive terms are smaller than the pair potential. Hence, we are going to neglect the external potential and the third particle potential in order to simplify our model. Thus, the inter-atomic interaction in our system is solely pair potential.

## 2.3 Description of Lennard-Jones potential

Lennard-Jones potential is a mathematical model which describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of separation. It was proposed by John Edward Lennard-Jones in 1924. This potential may not be a particularly accurate model for the interaction between rare gas atoms, but it has proved its worth in many other ways. Moreover, LJ clusters provide a useful testing ground for global optimization algorithms, partly because it is easily programmable.

It is remarkable that many of the global minimum structures have been observed experimentally for clusters of atoms and molecules covering a wide range of the periodic table [4].

This potential is given by (1) and consists of two terms: one of short-range repulsion ( $k/r^{12}$ ) and the other long-range attraction term ( $-k/r^6$ ). The repulsive term is stronger compared to the attractive term, which tends to zero as the particles move away. The potential has a unique minimum (for two particles), which in reduced units ( $\epsilon = \sigma = 1$ ) is equal to -1 at a distance  $2^{1/6}$ . In Figure 1 we can see the two particle Lennard-Jones potential.

Moreover, the repulsive term does not have a physical origin, its origin is purely mathematical that was adjusted to the experimental data. Instead, the attractive term has its origin in the quantum mechanics perturbation theory. To better understand the attractive term as a perturbation we can consider two atoms or molecules which interact. The electrons of each molecule will induce a dipole in the other one, this will rise to a dipole-dipole interaction. Applying perturbation theory to the ground state energy including both atoms

or molecules the first order correction will be zero and the second order will give us:

$$\Delta_n^{(2)} = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2 r^6} \frac{I_1 I_2}{I_1 + I_2}, \quad (8)$$

where  $I$  is the ionization energy for each atom, and  $\alpha$  the polarizability. Hence, the final result has the form  $-k/r^6$  which corresponds to the attractive term of Lennard-Jones potential [5].

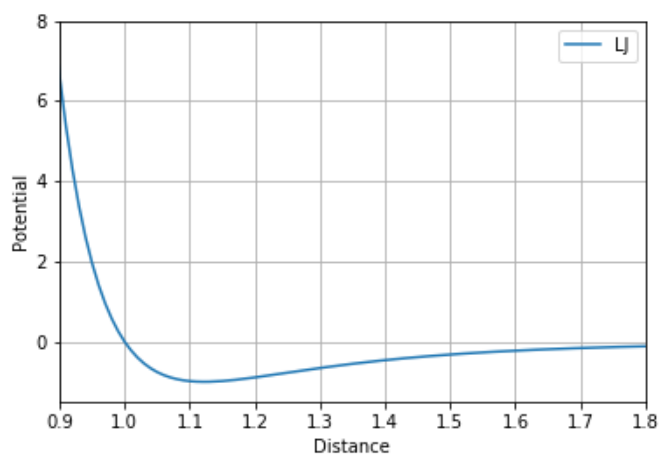


Figure 1: Representation of LJ potential in a two-particle system. Reduced units used ( $\epsilon = \sigma = 1$ )

## 2.4 Summary in Spanish

En primer lugar, para hacer un modelo que se ajuste a la realidad debemos escoger un potencial que concuerde con los datos experimentales. Un buen candidato es el potencial de Lennard-Jones el cual es un modelo matemático para un par de átomos neutros, gases nobles en nuestro caso. Este potencial consiste en un término repulsivo a corto alcance que no tiene origen físico, y un término atractivo a largo alcance cuyo origen está en la teoría de perturbaciones de la mecánica cuántica.

Además, un factor importante a tener en cuenta es el potencial electrónico creado por los electrones de cada átomo. Para ello utilizaremos la aproximación de Born-Oppenheimer de tal forma que podremos despreocuparnos de la interacción electrón-núcleo debido a la gran diferencia de masas entre ellos.

También hablaremos sobre la interacción interatómica, esto es, el potencial que usaremos vendrá dado únicamente por la interacción entre dos partículas (1)



sin tener en cuenta un potencial exterior o cómo una tercera partícula afecta al potencial entre ellas, ya que estas contribuciones.

### 3 Global Optimization Methods

In this section, three different global optimization methods will be introduced: Simulated Annealing (SA), Genetic Algorithm (GA) and Basin-Hopping (BH) algorithm. The advantages and disadvantages of these methods will be shown. The latter will be described in greater depth in the next chapter since it is the one used in this work.

#### 3.1 Simulated Annealing (SA)

Some optimization methods are based on natural processes. This is the case of Simulated Annealing where the system tries to simulate a dynamic system in which it can escape from the basins (local minima) in order to get trapped in ever lower minima. It was originally proposed for spin-glasses and combinatorial problems, but it was quickly applied to cluster science. This method tries to generate a random walk on the potential energy surface and uses Boltzmann probability to choose between two energies,  $E_1$  and  $E_2$ , to check if said energy or position over the PES is accepted or not. If  $E_1 > E_2$  the second energy is accepted, if  $E_2 > E_1$  is where the Boltzmann probability takes place and when this occurs it is compared with  $\delta$ , which is a randomly distributed number between 0 and 1

$$e^{-(E_2-E_1)/k_bT} > \delta. \quad (9)$$

This condition will make possible for the algorithm not to get stuck in a single minimum. The random walk is generated by the Metropolis algorithm. New states can be generated in various ways, one way is to perturb an atom or some of them according to some distribution of the step length and directions [2].

Typically the SA simulation starts at a high enough temperature so that the system is in a liquid state, and then slowly decreases logarithmically. Thus, when the temperature decreases and the system "solidifies" it is easier for it to be trapped in a local minimum.

The main drawback of SA is that as the temperature decreases and the system "solidifies" it is more likely that it will get stuck in a local minimum and will not find the global solution. One way to avoid this problem is decreasing the cooling rate.

#### 3.2 Genetic Algorithm (GA)

This type of algorithms, like SA are based on natural processes. In this case, GAs try to emulate natural selection processes. Genetic algorithms (GA) were

first theorized in the early 1950s with the work of Nils Aall Barricelli at the Institute for Advanced Study in Princeton, New Jersey. His work went unnoticed until John Holland's work gained popularity by publishing articles and finally a book [6] that laid the foundations for this type of algorithm in the early 1970s.

The GA is a search technique based on the principle of natural evolution. It uses operators that are analogues of the evolutionary processes of mating, mutation and natural selection to explore multi-dimensional parameter process [3].

This type of algorithm can be used when the variables to be optimized can be put in the form of a string, this string is called a chromosome. Each string is made up of genes that contain the variables to be optimized (alleles).

The initial population (first string or chromosome) is chosen randomly, sometimes can also be generated with previous knowledge about the system but we have to be careful not to over-condition so it is possible to obtain the optimized result correctly.

A very important concept of GA is fitness. It is a way of measuring the quality of test solutions or the initial population. A high fitness value corresponds to a high value of the function in the case of maximizing and to a low value of the function in the case of minimizing. In case of knowing the upper and lower values of the function, an absolute fitness can be established. Otherwise, we can use a dynamic fitness scale, where the fitness value of each individual is scaled according to the fitness of the current population.

Another important concept is selection. The two most commonly used methods to see which individuals in the population move to the next are the 'tournament selection' and 'roulette wheel'. The first method chooses some strings at random, the two with the highest fitness become the parents of the following population. The second method, a string is chosen randomly and it is compared with a random number between 0 and 1 if the fitness value is greater than that random number is chosen for the subsequent crossover. Otherwise, another string is chosen and the process is repeated.

The offspring will be the result of two (in some cases more than two) strings of greater fitness. There are different ways to produce offspring. Furthermore, another concept of importance is the mutation that brings genetic diversity to the population at random.

Thus, GA is a powerful algorithm that reduces computational time and the number of iterations or minimizations that it would normally take days for a random search algorithm to find the optimized solution.

### 3.3 Basin-Hopping Algorithm (BH)

The basin-hopping algorithm was first presented by D.J. Wales and J.P.K. Doye in 1997. This method is based on the PES transformation which does not change the global minimum, nor the energies of local minima [1]. It was the first unbiased search method to find the global minima up to 110 atoms for Lennard-Jones potential including  $LJ_{75}$  and  $LJ_{104}$  clusters, which are based on nonicosahedral structures.

### 3.4 Summary in Spanish

Los métodos de optimización son de gran importancia en muchas ramas de la ciencia. En esta sección presentamos los tres algoritmos más usados para encontrar el mínimo de energía global de un sistema. En estos sistemas el número de mínimos locales de la PES crece exponencialmente.

Uno de los algoritmos más interesantes es el algoritmo genético (GA) el cual se basa en la selección natural usando parámetros como la mutación, los parientes mejor preparados, etc. Otro algoritmo basado en un proceso natural es el simulated annealing (SA) o enfriamiento simulado, dicho método utiliza un decrecimiento paulatino de la temperatura del sistema estudiado, conforme la temperatura disminuye el sistema se queda atrapado en los mínimos locales de la superficie de energía potencial. Además, mientras baja la temperatura es más probable encontrar la solución global del sistema. El inconveniente de éste método es que conforme se enfría es fácil que se quede atrapado en un mínimo local y no acabe encontrando la solución global. Por último, el método utilizado en este trabajo es el basin-hopping (BH) el cual tiene un cierto parecido con el SA pero trabaja a una temperatura fija. Consiste en una transformación de la superficie de energía potencial (PES), que no modifica el mínimo global y suaviza la PES.

## 4 Basin-hopping algorithm

In the present work, basin-hopping algorithm is used for up to 55 noble gas atoms (neutral atoms) to obtain global minimum and so the most probable structure at low temperatures. To simplify the problem, classical Lennard-Jones potential (1) in reduced units have been used as mentioned above ( $\epsilon = \sigma = 1$ ).

### 4.1 Method followed

First, we generate randomly  $N$  particles within a sphere of radius 5, so we have an unbiased search. After that, a minimization routine is applied to the system

$$\tilde{V}(X) = \min(V(X)). \quad (10)$$

In (10),  $\tilde{V}$  is the transformed potential starting from the the  $3N$ - dimensional vector of the nuclei  $X$ . So, (10) is applied to every new configuration.

After each minimization we apply a perturbation to each of the  $3N$  coordinates. We must ensure that this perturbation is not large enough so that no particles remain outside the sphere, nor small enough that it remains in the same local minimum. The perturbation used in this work, in reduced units, is given by

$$X_{i+1} = X_i + 2\delta(\text{ran} - 0.5), \quad (11)$$

where  $\delta$  is the maximum displacement of the particles and  $\text{ran}$  is a uniformly distributed random number between 0 and 1. Thus, the new state and the state

before the perturbation are compared according to Boltzmann probability (9) similarly done in simulated annealing. This will allow us, as mentioned above, even though the global minimum has been found to continue traveling the PES due to its stochastic character.

We repeat the process until the number of steps ( $n$ ) set at a fixed temperature ( $T$ ) is reached. In each step, a minimization is performed from the perturbation on each of the coordinates. When the total number of steps is performed we are left with the minimum energy obtained from all the iterations. To check each of the results, The Cambridge Energy Data Landscape has been used. [7]

These types of algorithms usually take a long time to complete since they must make many calls to the same function in order to optimize it. In order to make the program faster, we must optimize the code as much as possible, such as eliminating unnecessary loops and conditionals, reserving memory for the results instead of creating memory as the program progresses, etc. But there are physical parameters that also influence the speed of execution of the program such as temperature ( $T$ ).

The best way to choose the correct temperature is to run the algorithm for the same cluster at different temperatures and see how many steps it has taken to find the global minimum. The temperature was set to 0.8 for all clusters, which is probably not the most optimal for each cluster.

Another very important point to decrease the computational time is the minimization routine used. In this work, the routine L-BFGS-B has been used, which is a quasi-Newton method which approximates Broyden – Fletcher – Goldfarb – Shanno algorithm using a limited amount of computer memory. This algorithm is used for constrained systems where upper and lower bounds are known. Also uses a scalar and differentiable function  $f$ . To make this method even faster, we must provide the analytical derivative of this function, otherwise it calculates the derivative numerically, considerably increasing the computational time.

## 4.2 Energies obtained

The energies for the first clusters ( $N = 2,3,4$ ) can be found trivially by  $-N(N - 1)/2$  since all the particles can be placed at the minimum equilibrium distance that is -1 in reduced units [2]. From  $N = 5$  onwards the energies are strictly greater than the trivial solution.

Our method, based on the basin-hopping algorithm, was able to find the global minima for all clusters up to  $N = 55$  in the first run with 5000 steps. The only exception was  $LJ_{38}$  which was found in the second run. In the first run for  $LJ_{38}$  cluster was done with 10000 steps and with a maximum displacement of the particles ( $\delta$ ) equal 0.6, which led us to the solution of an icosahedral local minimum while the second run, with  $\delta$  equal to 0.4 and 20000 steps led us to the nonicosahedral global minimum. This structures will be discussed in the next section.

As mentioned above, what is going to allow us to distinguish between a useful and an invalid method is the ability to find the global minima for  $LJ_{38}$

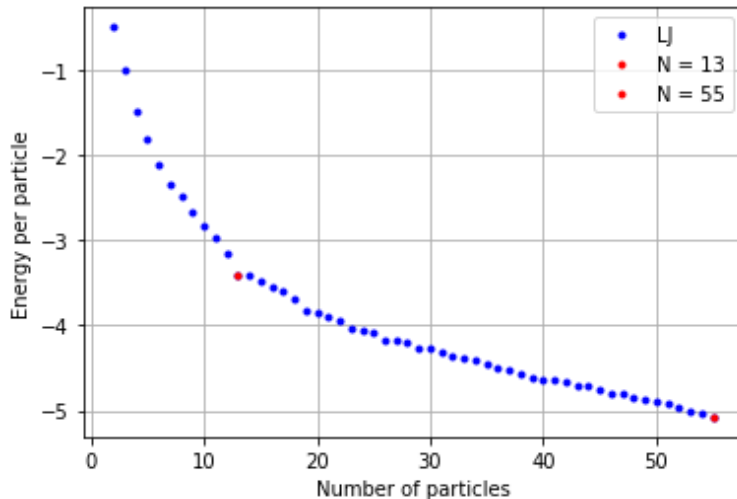


Figure 2: Energy per particle. Red dots correspond to complete Mackay icosahedra.

and  $LJ_{75}$ . The first one has been found satisfactorily.

In Figure (2) a representation of the energy per particle up to  $N = 55$  is shown, where we can see how some points get out of the trend line and which correspond to especially stable structures compared to neighboring clusters.

### 4.3 Summary in Spanish

En esta sección se explica el funcionamiento del método usado (BH) y todos los pasos seguidos durante el proceso. Se explica la generación aleatoria de los  $N$  átomos, la perturbación inducida al sistema tras la minimización, y también, la rutina de minimización usada en el proceso. Además, se exponen algunas formas para disminuir el tiempo computacional y ajustar parámetros físicos como la temperatura ( $T$ ). Por último, se expone un resumen de las energías obtenidas hasta el  $N = 55$ .

## 5 Results and discussions

In this section the most predominant structures and their stability in the range of  $N = 10 - 110$  will be discussed. Moreover, there are some interesting cases that do not follow the same pattern as the other clusters. Some examples will be shown with images of the most interesting results studied in the work.

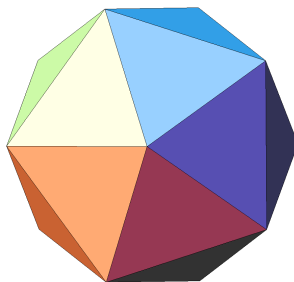


Figure 3: Regular convex icosahedra

## 5.1 Stability

In order to know the stability of the studied clusters, a well-known parameter is the second-order energy difference. This is given by

$$\Delta_2 E(N) = E(N + 1) + E(N - 1) - 2E(N). \quad (12)$$

In the Figure (4) we can see this parameter for  $N$  up to 55 atoms. The maxima of the graph are the clusters that are especially stable. Moreover, the two red dots in Figure (4) and Figure(2) represent the most stable clusters which correspond with a complete Mackay icosahedra geometry as we will see in the next section. They can give us a notion about the "magic numbers" which are observed in mass spectrum for neutral atoms like Argon clusters for example.

## 5.2 Icosahedral structures

As mentioned in the previous section, cases  $N = 2,3,4$  are trivial solutions and their structure corresponds respectively to a dimer, equilateral triangle, and regular tetrahedron, with all inter-atomic distances equal to  $2^{1/6}$  [2]. It should also be noted that in the range of  $N = 10 - 110$  the most predominant structure is the Mackay icosahedron [1]. Icosahedron is a polyhedron with 20 faces, 30 edges and 12 vertices (Figure 3).

Many different clusters can be described as layers of close-packed atoms stacked on top of each other. The two most commonly encountered cubic close-packing schemes are the hexagonal-close-packed (hcp) and face-centered-cubic (fcc) [4]. In Figure 5 we can see Mackay and anti-Mackay sequences which correspond to fcc and hcp respectively.

A complete Mackay icosahedron is given by the formula

$$\frac{1}{3}(10n^3 + 15n^2 + 11n + 3), \quad (13)$$

where  $n$  is a natural number [4]. Hence, complete Mackay icosahedron are given for the sequence  $N = 13,55,147,309\dots$ . These clusters have greater stability than the rest of the structures studied as we can see in Figure (4). The most

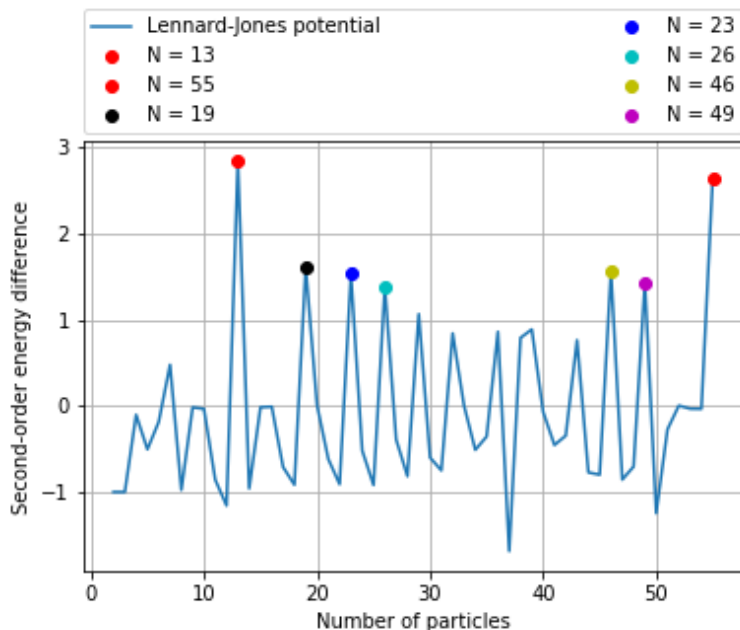


Figure 4: Second-order energy difference for up to 55 particles. Red dots correspond to complete Mackay icosahedra. Rest of the dots correspond to especially stable clusters.

stable clusters studied are those who form a complete Mackay icosahedra and they do not present big difficulty to find the global minimum.

As an example, the 13 atoms cluster has 1 328 isomers from which the lowest is the icosahedron with an energy of -44.327 (Figure (6)). The first excited state has an energy of -41.472 and it is obtained from icosahedron promoting one atom to the next shell and relaxing the resulting vacancy. Therefore, the density of states for the 13 atom cluster has a large "gap" that separates the icosahedron from the rest of the local minima [2]. This gap gives us the reason of its stability.

Something similar occurs with the  $N = 55$ , the global minimum, figure (7), is at -279.248 and the next local minimum is at an energy of -276.604 . As we can notice, there is a "gap" between these minima which will lead to great stability for said cluster. Both minima correspond to a Mackay icosahedron, but the second has an excited atom which is promoted to the next shell.

There are some clusters that even if they may not be the most stable structures their stability is interesting (Figure 4) and their structure will be shown. These clusters correspond to  $N = 19, 23, 26, 46$  and  $49$ . All figures are exposed in Appendix A.

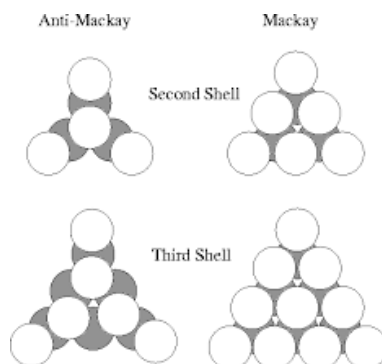


Figure 5: Mackay and anti-Mackay cubic close-packing schemes.[4]

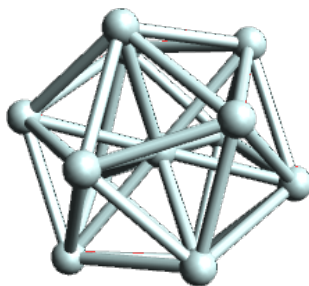


Figure 6: Geometry given by the global minimum for  $N = 13$ . Image represented by the program Avogadro. [8]

### 5.3 Nonicosahedral structures

There are also structures in which the shape is nonicosahedral. These structures are the perfect test to see if the optimization method used is effective or not. The first example is found in  $LJ_{38}$  cluster, where the structure that is formed in the global minimum is a truncated octahedron (hcp) with a over-layer that is unstable, as we can see in Figure (8). The second lowest minimum gives rise to an icosahedra geometry that we can see in Figure (9).

### 5.4 Summary in Spanish

En esta sección trataremos las distintas estructuras formadas en los mínimos globales de los diferentes agregados. La gran mayoría de estos están basados en el icosaedro y dichas geometrías son mucho más fáciles de encontrar que las que no lo están.

Los casos en los que la geometría es no icosaedra son casos particulares muy útiles para poner a prueba el método utilizado, pues dichos estructuras son



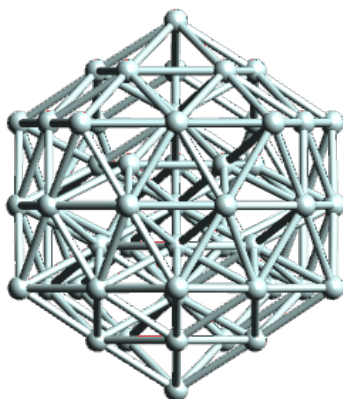


Figure 7: Geometry given by the global minimum for  $N = 55$ . Image represented by the program Avogadro. [8]

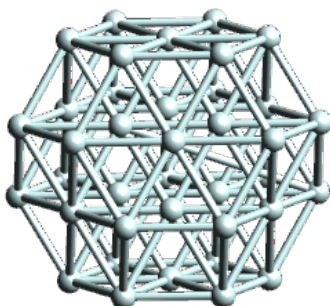


Figure 8: Geometry given by the global minimum for  $N = 38$ . Image represented by the program Avogadro. [8]

muy difíciles de encontrar. También trataremos de justificar la estabilidad de cada agregado con la diferencia de energía a segundo orden.

## 6 Conclusion

The method used in the present work based on the basin-hopping algorithm has been able to find the global minima for each cluster up to  $N = 55$ . Thus, we can say the result obtained were good but there several things that could improve our method.

Surely the most effective method to improve our program would be to adjust some parameters like temperature and the maximum displacement of the atoms, since they are very important for the speed of the program. This could be carried out by introducing an acceptance parameter that every  $n$  (100 steps, for

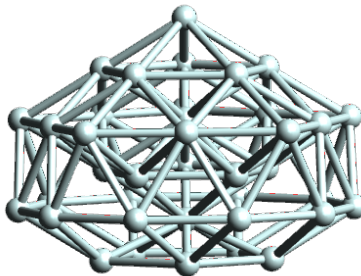


Figure 9: Geometry given by the second lowest minimum for  $N = 38$ . Image represented by the program Avogadro. [8]

example) steps multiplies by a factor that lowers or raises the temperature, the same could be done with the maximum displacement.

We might think that a hybrid method, such as BH combined with SA could be a valid model, but it has been shown that this method has problems with some clusters with few atoms.

Another way to improve the algorithm would be to implement it jointly with the Genetic Algorithm, which is very fast and useful method if implemented correctly. As proposed by R. Huang et al. recently "Subsequently, the performance evaluation shows that the introduction of GA markedly improves the convergent speed of the BHGA (Basin Hopping Genetic Algorithm) and the possibility for finding the global minima on the PES in comparison with the standard BH method" [9]. It is a BH based method where when the minimization routine at any step is done is where the GA makes the difference choosing between the fittest "parents".

The field of global optimization of complex systems is a field of great interest and in continuous development, as it allows us to find solutions to problems of many degrees of freedom. The goal is to create algorithms as fast as natural processes such as protein folding. Hence, Lennard-Jones clusters are a very effective way to test these methods due to their simplicity to be programmed and the complexity of some clusters such as  $LJ_{38}$  or  $LJ_{75}$ .

## 6.1 Summary in Spanish

El método de optimización usado en este trabajo ha sido capaz de encontrar los mínimos globales de todos los agregados hasta el  $N = 55$ . Por tanto, podemos concluir que el trabajo se ha realizado de forma satisfactoria pues ha sido capaz de reproducir los datos del Cambridge Energy Landscape Database [7], aunque hay varios puntos en los que se puede mejorar.

La formas más inmediata sería implementar un paso y una temperatura variables. Otra forma alternativa, pero probablemente más eficaz, es la de hacer un programa que mezcle el GA con BH, como se ha propuesto en trabajos recientes.

Por último, cabe destacar que este tipo de métodos son muy útiles y son una rama abierta sobre la que investigar pues son capaces de resolver problemas de muchos grados de libertad. Por tanto, los agregados de Lennard-Jones son una primera prueba muy efectiva para ver la utilidad de dichos métodos.

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## A Icosahedral structures

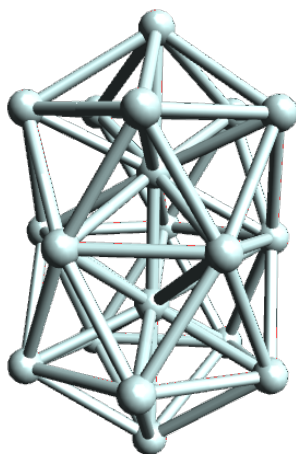


Figure 10: Geometry given by the global minimum for  $N = 19$ . Image represented by the program Avogadro. [8]

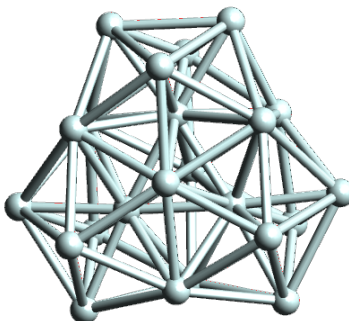


Figure 11: Geometry given by the global minimum for  $N = 23$ . Image represented by the program Avogadro. [8]

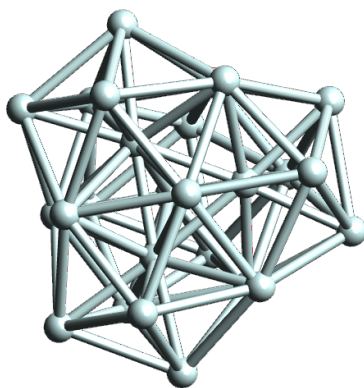


Figure 12: Geometry given by the global minimum for  $N = 26$ . Image represented by the program Avogadro. [8]

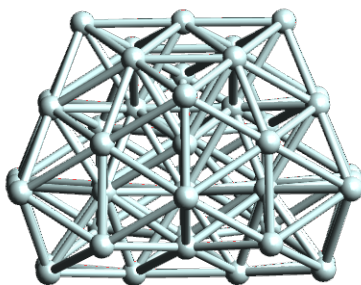


Figure 13: Geometry given by the global minimum for  $N = 46$ . Image represented by the program Avogadro. [8]

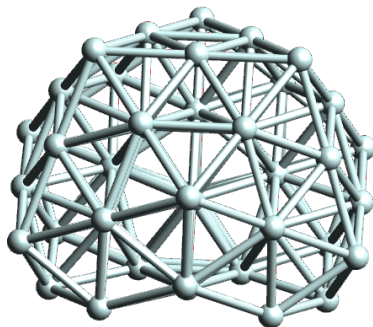


Figure 14: Geometry given by the global minimum for  $N = 49$ . Image represented by the program Avogadro. [8]