Department of Physics

Global Optimization in Complex Systems

Final Degree Project

Author:
Kiril Ivanov Kurtev

Supervisor:
Dr Javier Hernández Rojas

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Contents

List of Figures

1 Introduction

Global optimization is a eld of great interest in many di erent branches of science. The objective of global optimization is to nd 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, nancial planning, process control, risk management, scienti c modeling, and others. However, this work is going to focus on the optimization of a cluster composed by rare gases atoms.

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

$$V_{LJ} = 4 \sum_{i<j} [(\frac{}{r_{ij}})^{12} \quad (\frac{}{r_{ij}})^{6}]; \tag{1}$$

where r_{ij} is the distance between the i-th and j-th particle, and $2^{1=6}$ 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], nding the global minimum can be very di cult. 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 di cult to nd 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 su ciently high temperatures performs several iterations at a xed 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 e cient 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 optimizacion global de sistemas complejos es un campo de gran interes en distintas ramas de la ciencia. El objetivo de la optimizacion global es encontrar el mínimo global de energía de un sistema, en la mayoría de los casos basado en un modelo no linear, en presencia de muchos mínimos locales. Esto es util en campos como la economía, ciencias naturales o ingeniería. En este trabajo trabajaremos con agregados de gases nobles para encontrar la estructura mas probable a bajas temperaturas.

Para ello, usaremos un modelo de interaccion entre los atomos basado en el potencial de Lennard-Jones. La interaccion entre todos los atomos dara lugar a una superficie de energía potencial cuyo mínimo global está íntimamente ligado con la estructura mas probable que formara el agregado.

Por otro lado, presentaremos los tres metodos mas usados para resolver este tipo de problemas, mostrando sus puntos fuertes y sus inconvenientes. Estos algoritmos son: algoritmo genetico (GA), enfriamiento simulado (SA) y el algoritmo de basin-hopping (BH). Este trabajo se centrara en este utlimo, el BH.

Por ultimo, presentaremos los resultados obtenidos y discutiremos la utilidad del trabajo, ademas de proponer algunas mejoras para futura continuacion 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 Schrodinger's equation for a molecule with n electrons, mass m_e and N nuclei with masses M_t is

$$[\sum_{t=1}^{N} \frac{h^2}{2M_t} r_t^2 \sum_{i=1}^{n} \frac{h^2}{2m_e} r_i^2 + V(x;X)] \quad (x;X) = E_{TOTAL} \quad (x;X); \qquad (2)$$

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

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

$$V(x;X) = \frac{e^2}{4 \quad _0}[\sum_{i;t}^{nN} \frac{Z_t}{r_{it}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{t<s} \frac{Z_t Z_s}{r_{ts}}]; \qquad (3)$$

where Z_t is the atomic number of nucleus t, e is the charge of the proton. $r_{it} = jx_i \quad X_t j$ where x_i is the vector position of the electron i and X_t, the vector position of the nucleus t. Thus, the rst 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:

$$(x;X) = \quad _e(x;X) \quad _n(X); \qquad (4)$$

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

$$[\hat{H} \quad \hat{T}_n] \quad _e(x;X) = V_e(X) \quad _e(x;X); \qquad (5)$$

$\hat{H}$ is the total Hamiltonian operator, and $\hat{T}_n$ is the nuclear kinetic energy operator (rst term of equation (2)). Thus, we write $\quad _e(x;X)$ and $V_e(X)$ to show that di erent electronic wavefunctions and energies are obtained for di erent nuclear con gurations.

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

Finally, the appropriate Schrodinger equation for the nuclear wavefunction, $_n(X)$, is

$$[\hat{p}_n + V_e(X)] \quad _n(X) = E_{TOTAL} \quad _n(X): \tag{6}$$

2.2 Inter-atomic interaction

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

$$U(\vec{r}_1; \vec{r}_2; :::; \vec{r}_N) = \sum_i U_1(\vec{r}_i) + \sum_i \sum_{j<i} U_2(\vec{r}_i; \vec{r}_j) + \sum_i \sum_{j<i} \sum_{k<j} U_3(\vec{r}_i; \vec{r}_j; \vec{r}_k) + :::; \tag{7}$$

where U_1 is the external potential that a ects 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 a ects 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 (= = 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 rst order correction will be zero and the second order will give us:

$$^{(2)}_{n} = \frac{3}{2}\frac{^{1\ 2}}{(4\ _0)^2 r^6}\frac{I_1 I_2}{I_1 + I_2}; \tag{8}$$

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

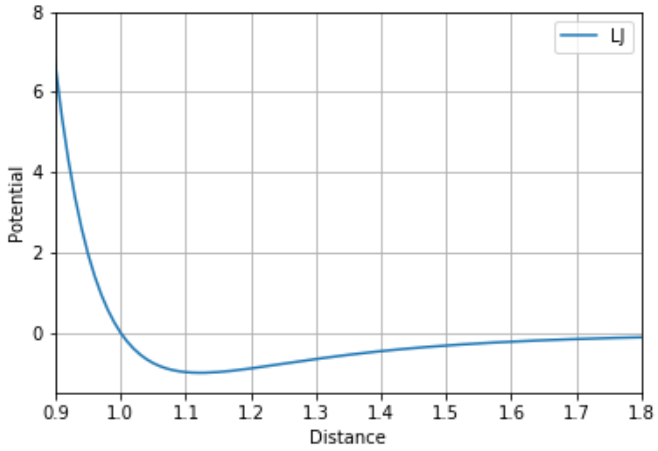

Figure 1: Representation of LJ potential in a two-particle system. Reduced units used (= = 1)

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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 matematico para un par de atomos neutros, gases nobles en nuestro caso. Este potencial consiste en un termino repulsivo a corto alcance que no tiene origen f sico, y un termino atractivo a largo alcance cuyo origen esta en la teor a de pertubaciones de la mecanica cuantica.

Ademas, un factor importante a tener en cuenta es el potencial electronico creado por los electrones de cada atomo. Para ello utilizaremos la aproximacion de Born-Oppenheimer de tal forma que podremos despreciar la interaccion electron-nucleo debido a la gran diferencia de masas entre ellos.

Tambien hablaremos sobre la interaccion interatomica, esto es, el potencial que usaremos vendra dado unicamente por la interaccion entre dos part cula (1)

sin tener en cuenta un potencial exterior o como una tercera part cula afecta al potencial entre ellas, ya que estas contrubiciones.

3 Global Optimization Methods

In this section, three di erent 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 , which is a randomly distributed number between 0 and 1

$$e^{(E_2 \quad E_1)=k_b T} > : \tag{9}$$

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 "solidi es" 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 "solidi es" it is more likely that it will get stuck in a local minimum and will not nd 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

rst 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 nally 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 (rst 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 tness. It is a way of measuring the quality of test solutions or the initial population. A high tness 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 tness can be established. Otherwise, we can use a dynamic tness scale, where the tness value of each individual is scaled according to the tness 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 rst method chooses some strings at random, the two with the highest tness 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 tness value is greater than that random number is chosen for the subsequent crossover. Otherwise, another string is chosen and the process is repeated.

The o spring will be the result of two (in some cases more than two) strings of greater tness. There are di erent ways to produce o spring. 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 nd the optimized solution.

3.3 Basin-Hopping Algorithm (BH)

The basin-hopping algorithm was rst 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 rst unbiased search method to nd 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 metodos de optimizacion son de gran importancia en muchas ramas de la ciencia. En esta seccion presentamos los tres algoritmos mas usados para encontrar el m nimo de energ a global de un sistema. En estos sistemas el numero de m nimos locales de la PES crece exponencialmente.

Uno de los algoritmos mas interesantes es el algoritmo genetico (GA) el cual se basa en la seleccion natural usando parametros como la mutacion, los parientes mejor preparados, etc. Otro algoritmo basado en un proceso natural es el simulated annealing (SA) o enfriamiento simulado, dicho metodo utiliza un decrecimiento paulatino de la temperatura del sistema estudiado, conforme la temperatura disminuye el sistema se queda atrapado en los m nimos locales de la super cie de enrg a potencial. Ademas, mientras baja la temperatura es mas probable encontrar la solucion global del sistema. El inconveniente de este metodo es que conforme se enfr a es facil que se quede atrapado en un m nimo local y no acabe encontrando la solucion global. Por ultimo, el metodo utilizado en este trabajo es el basin-hopping (BH) el cual tiene un cierto parecido con el SA pero trabaja a una temperatura ja. Consiste en una transformacion de la super cie de energ a potencial (PES), que no modi ca el m nimo 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 (= = 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

$$\nabla(X) = min(V(X)): \tag{10}$$

In (10), ∇ is the transformed potential starting from the the $3N$- dimensional vector of the nuclei X. So, (10) is applied to every new con guration.

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

$$X_{i+1} = X_i + 2\ (ran \quad 0{:}5); \tag{11}$$

where is the maximum displacement of the particles and 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 xed 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 in uence 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 di erent temperatures and see how many steps it has taken to nd 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 di erentiable 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 rst 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 nd the global minima for all clusters up to N = 55 in the rst run with 5000 steps. The only exception was LJ_{38} which was found in the second run. In the rst run for LJ_{38} cluster was done with 10000 steps and with a maximum displacement of the particles ( ) equal 0.6, which led us to the solution of an icosahedral local minimum while the second run, with 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 nd the global minima for LJ_{38}

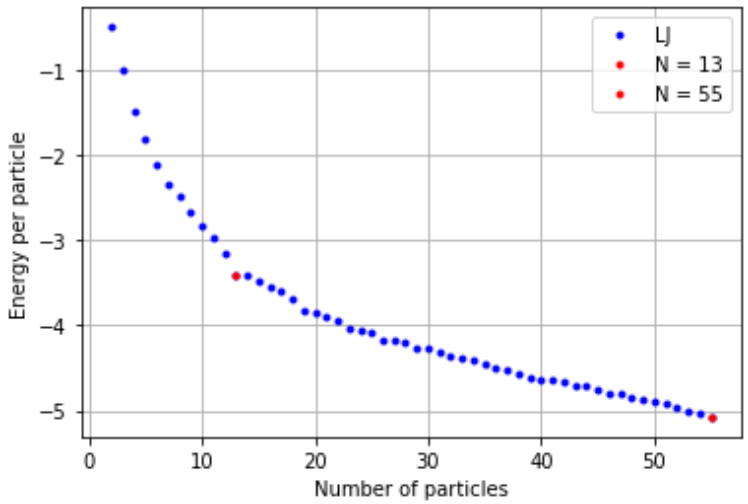

Figure 2: Energy per particle. Red dots correspond to complete Mackay icosahedra.

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 seccion se explica el funcionamiento del metodo usado (BH) y todos los pasos seguidos durante el proceso. Se explica la generacion aleatoria de los N atomos, la perturbacion inducida al sistema tras la minimizacion, y tambien, la rutina de minimizacion usada en el proceso. Ademas, se exponen algunas formas para disminuir el tiempo computacional y ajustar parametros fsicos como la temperatura (T). Por ultimo, se expone un resumen de las energ as 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.

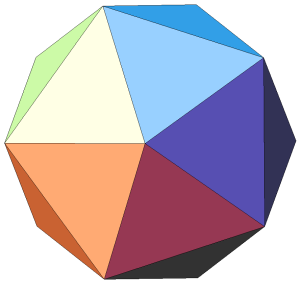

Figure 3: Regular convex icosahedra

5.1 Stability

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

$$_2E(N) = E(N + 1) + E(N \quad 1) \quad 2E(N): \tag{12}$$

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 di erent 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

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

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

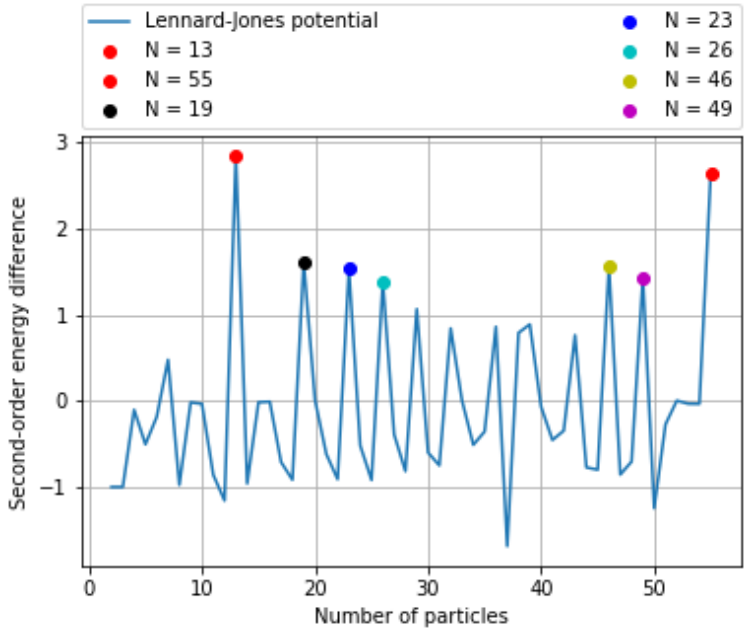

Figure 4: Second-order energy di erence for up to 55 particles. Red dots correspond to complete Mackay icosahedra. Rest of the dots correspond to especially stable clusters.

stable clusters studied are those who form a complete Mackay icosahedra and they do not present big di culty to nd 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 rst 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, gure (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 gures are exposed in Appendix A.

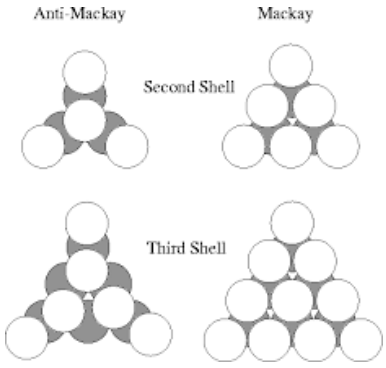

Figure 5: Mackay and anti-Mackay cubic close-packing schemes.[4]

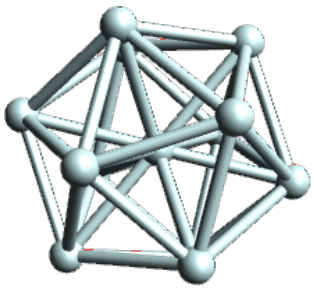

Figure 6: Geometry given by the global minimum for N = 13. Image represented by the program Avogadro. [8]

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 e ective or not. The rst 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 seccion trataremos las distintas estructuras formadas en los m nimos globales de los diferentes agregados. La gran mayor a de estos estan basados en el icosahedro y dichas geometr as son mucho mas faciles de encontrar que las que no lo estan.

Los casos en los que la geometr a es no icosahedra son casos particulares muy utiles para poner a prueba el metodo utilizado, pues dichos estructuras son

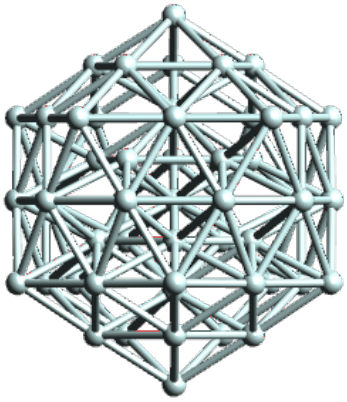

Figure 7: Geometry given by the global minimum for N = 55. Image represented by the program Avogadro. [8]

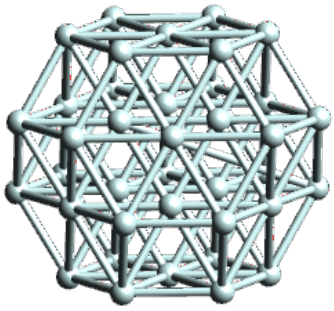

Figure 8: Geometry given by the global minimum for N = 38. Image represented by the program Avogadro. [8]

muy dif ciles de encontrar. Tambien trataremos de justi car la estabilidad de cada agregado con la diferencia de energ a a segundo orden.

6 Conclusion

The method used in the present work based on the basin-hopping algorithm has been able to nd 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 e ective 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

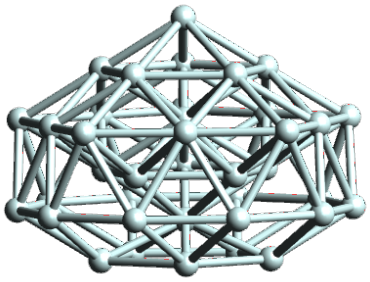

Figure 9: Geometry given by the second lowest minimum for N = 38. Image represented by the program Avogadro. [8]

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 metodo de optimizacion 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 reporoducir los datos del Cambridge Energy Landscape Database [7], aunque hay varios puntos en los que se puede mejorar.

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

Por ultimo, cabe destacar que este tipo de metodos son muy utiles 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 metodos.

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A Icosahedral structures

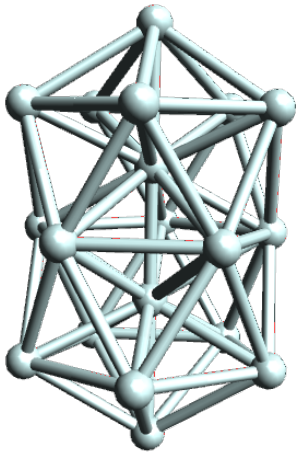

Figure 10: Geometry given by the global minimum for N = 19. Image represented by the program Avogadro. [8]

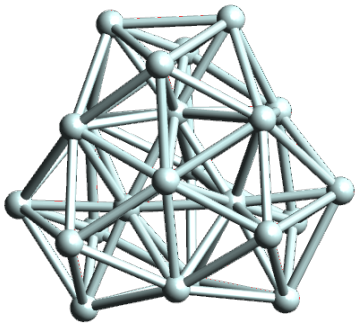

Figure 11: Geometry given by the global minimum for N = 23. Image represented by the program Avogadro. [8]