

**Optical and Thermodynamic  
properties of noble metal  
nanoparticles.  
Effect of chemical  
functionalization.**

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# Objective

This laboratory is intended to introduce the student to the use of semiempirical electronic structure methods. In particular, the semiempirical methods will be applied to the study of metallic clusters and the interaction of the clusters with molecules such as pyridine. The reactivity of the metallic systems will be rationalized in terms of the electron populations in the cluster. Optical properties and the metal-ligand affinity will be quantitatively estimated.

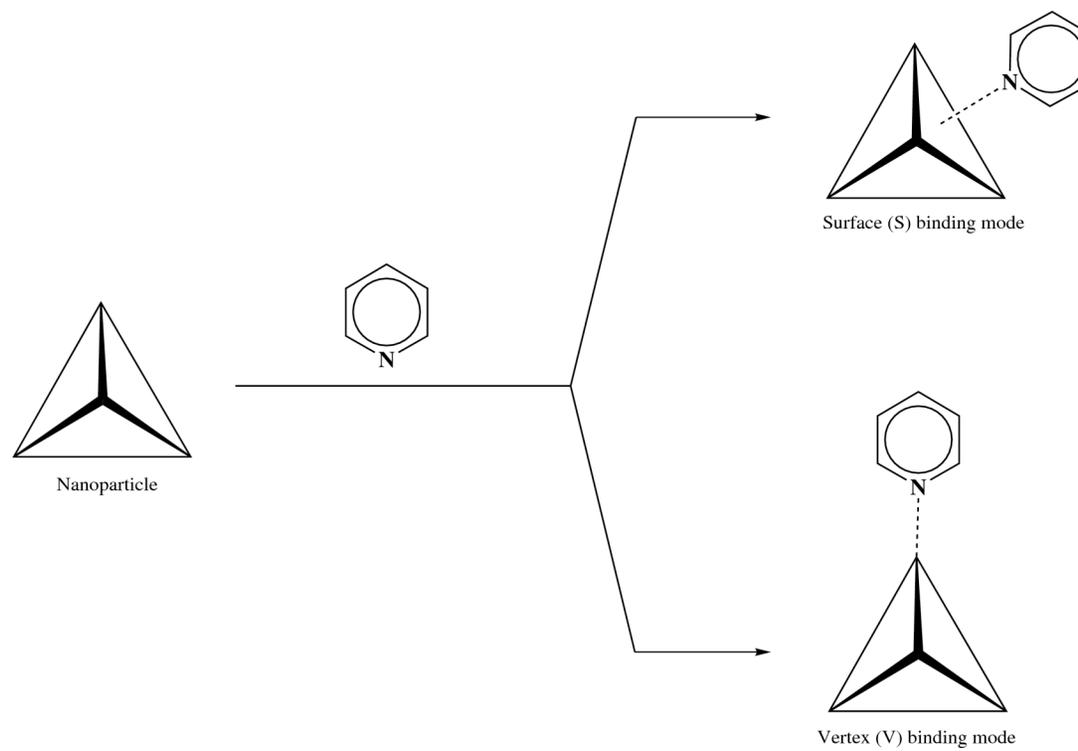
# Introduction

•The noble metals nanoparticles (Cu, Ag and Au) exhibit physical properties that make them unique for scientific and technological applications: electronics, catalysis, biotechnology, spectroscopy, etc. These properties may be modulated by specific chemical treatment of the particles during their synthesis. Hence, the geometrical and electronic characterization of their structures is crucial to understand the mechanisms that control such properties.

•In this exercise, we will use a theoretical approach to study nanoparticles of Silver and Gold; including their structural and optical properties and the changes in these properties that arise from chemical functionalization. In order to assess the quality of our calculations it is common to contrast the results with other theoretical studies based on similar models.<sup>1</sup> Thus, we will consider structures of tetrahedral/pyramidal shape whose geometries –interatomic distances and angles– have been taken from their natural crystal lattices.<sup>2</sup>

•The affinity of the metal particles for other chemical species will be calculated by the difference in energy between the isolated molecules and the aggregate. shows a schematic representation of the two binding modes of interaction between pyridine and a metal particle of pyramidal shape. With this schematic in mind, we will identify the reactive sites of the metal particles and study which mechanism is thermodynamically favored. The optical properties of different molecule-cluster systems will also be investigated.

**Gold:** Aikens, C. M.; Schatz, G. C. J. Phys. Chem, A 2006, 110, 13317. **Silver:** Zhao, L.; Jensen, L.; Schatz, G. C. J. Am. Chem. Soc. 2006, 128, 2911.  
**Silver:** Wyckoff, R. W. G. Crys. Struct. 1963, 1, 7. **Gold:** (a) Straumanis, M. E. Monatsh. Chem. 1971, 102, 1377. (b) Suh, I.-K.; Ohta, H.; Waseda. Y. J. Mater. Sci. 1988, 23, 757.



**Figure 1.-** Representation of the two binding modes of a donor ligand (pyridine) to a metal particle of tetrahedral shape. In the *S* mode the pyridine attaches to a surface of the particle while in the *V* mode it reacts with the vertices.

# Procedure

For this particular exercise we will use the program CNDO/INDO accessible at the [NanoHUB](#) (Figure 2). The following is a direct link to the application [CNDO/INDO](#). The atomic coordinates of the species that we will study on this tutorial are available on-line.

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Workspace (800x600)		
CNDO/INDO		
Molecular Structure Tracer		

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**Figure 2.-** NanoHUB window showing *My HUB*. The programs are listed on the tab *All Tools* of the menu *My Tools*. Selecting the star next to the name of the desired tool, marks it as *Favorite* and a link to it is placed in the *Favorites* folder. The button launches the application.

## The CNDO/INDO program interface

### 1.- The CNDO/INDO program interface.

After logging into the nanoHUB, select the option *My HUB* (see Figure2). On the menu *My Tools* select the tab *All Tools* and locate the application CNDO/INDO. If you click on the star next to the name, the application will be marked as *Favorite* and placed in the *Favorites* folder.<sup>3</sup>

At this point you may start the application by clicking on the *Launch Tool* button. The window with the program's GUI will appear as illustrated in Figure 3. The *Popout* feature of the tool (located on the upper right hand side of the window) may be activated by clicking on the button; it will create a dedicated window to the tool on your local computer that facilitates the work.<sup>4</sup>

If you wish to continue working on the current project from a different location or computer, you may close the browser and even shut down the computer; when you log back into the NanoHUB all be as you left it. Even if a job was running, it will continue running on the background or, most likely, it will have finished the calculation in the meantime. Do not however click on the *Close* button, unless you wish to terminate the current CNDO/INDO session for good.

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(3) Alternatively, you may call the program directly, [www.nanohub.org/tools/cndo](http://www.nanohub.org/tools/cndo), or through the utility NUITNS (Northwestern University Initiative for Teaching NanoScience). The package NUITNS is located on [www.nanohub.org/tools/nuitns](http://www.nanohub.org/tools/nuitns) and provides access to a group of complementary programs aimed to the study of molecular systems by electronic structure methods.

(4) To reattach the window to the browser click again on the *Popout* button.

nanoHUB.org – Middleware: Invoke: CNDO/INDO

https://nanohub.org/mw/invoke/cndo\_r26?appcaption=CNDO%2FINDO&version=26

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**CNDO/INDO** Storage 40%

Tool Questions? About Refresh Window Popout Close

CNDO Job: Pyridine

Molecular System Control Parameters Hamiltonian Parameters Interaction Factors Configuration Interaction Output

Charge: 0

Spin

Multiplicity: 1

Spin Scheme

Mode: Low Spin

Electrons: 0

Orbitals: 0

Geometry Specification

Point Group: Auto

Units: Angstroms

Atomic Positions:

N	7.0	0.000000	0.000000	1.400000
C	6.0	1.212436	0.000000	0.700000
C	6.0	1.212436	0.000000	-0.700000
C	6.0	0.000000	0.000000	-1.400000
C	6.0	-1.212436	0.000000	-0.700000
C	6.0	-1.212436	0.000000	0.700000

Simulate >

1193 x 582

Share session with:   Read-Only?  (Session is currently not shared.)

**Figure 3.-** Initial window of the CNDO/INDO program interface on the web browser.

## 2.- Definition of the model.

### 2a.- Molecular geometry, electric charge, and spin multiplicity.

To illustrate the use of the CNDO/INDO program, let us consider the Au<sub>20</sub> cluster, a gold nanoparticle with a pyramidal shape. The structure, extracted from the experimental, X-ray structure of the material, is given in Cartesian coordinates in the file Au20.xyz located on the directory “Assignments/CA/NanoParticles/Au” on Blackboard. Download the file to your computer and then upload the coordinates to the CNDO/INDO program: on the *CNDO Job* menu, located on main window of the tool (see ), select *Upload...* and follow the instructions to pass the Au20.xyz file to the CNDO/INDO program. The Cartesian coordinates of the cluster will appear on the text box *Atomic Positions*. The interatomic distances are in Angstroms so the *Units* option must be set accordingly. During the computation, we will ignore the symmetry of the system so select option “C1” for the *Point Group*.

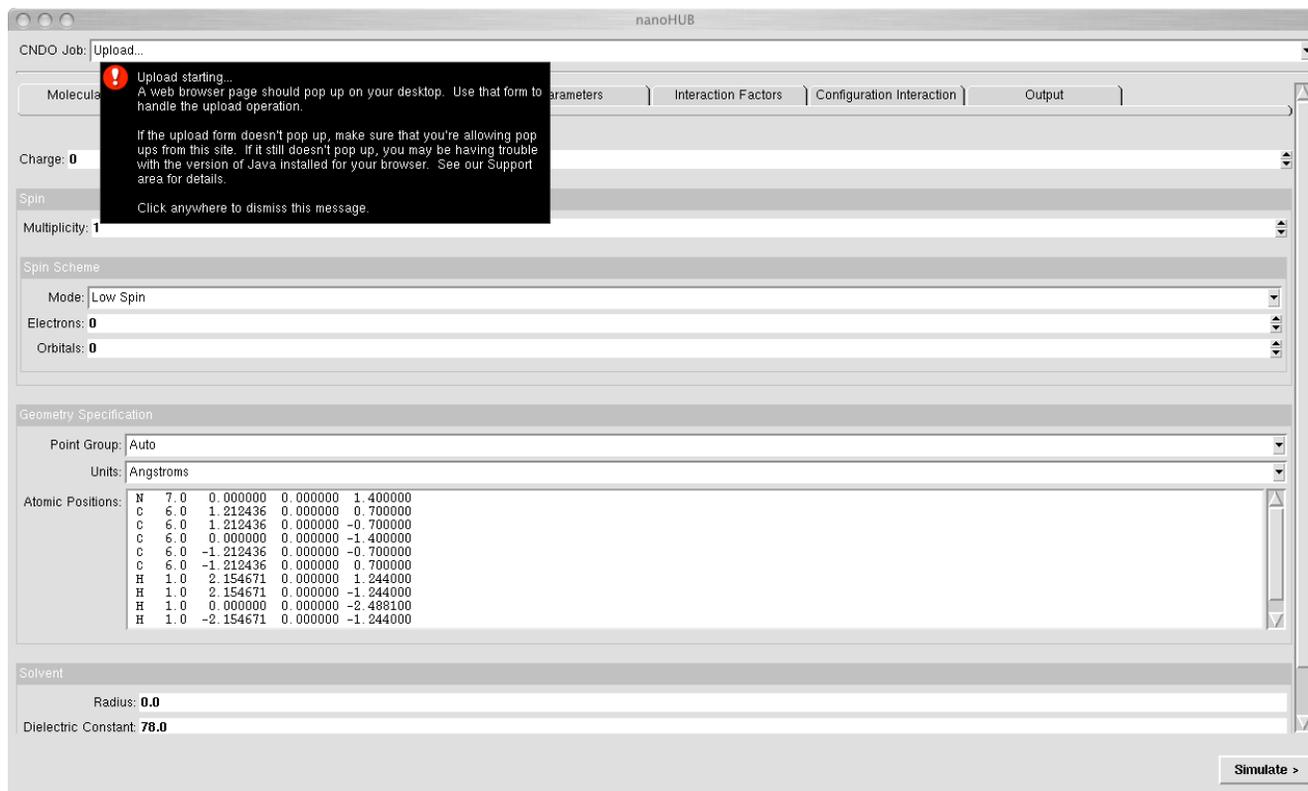
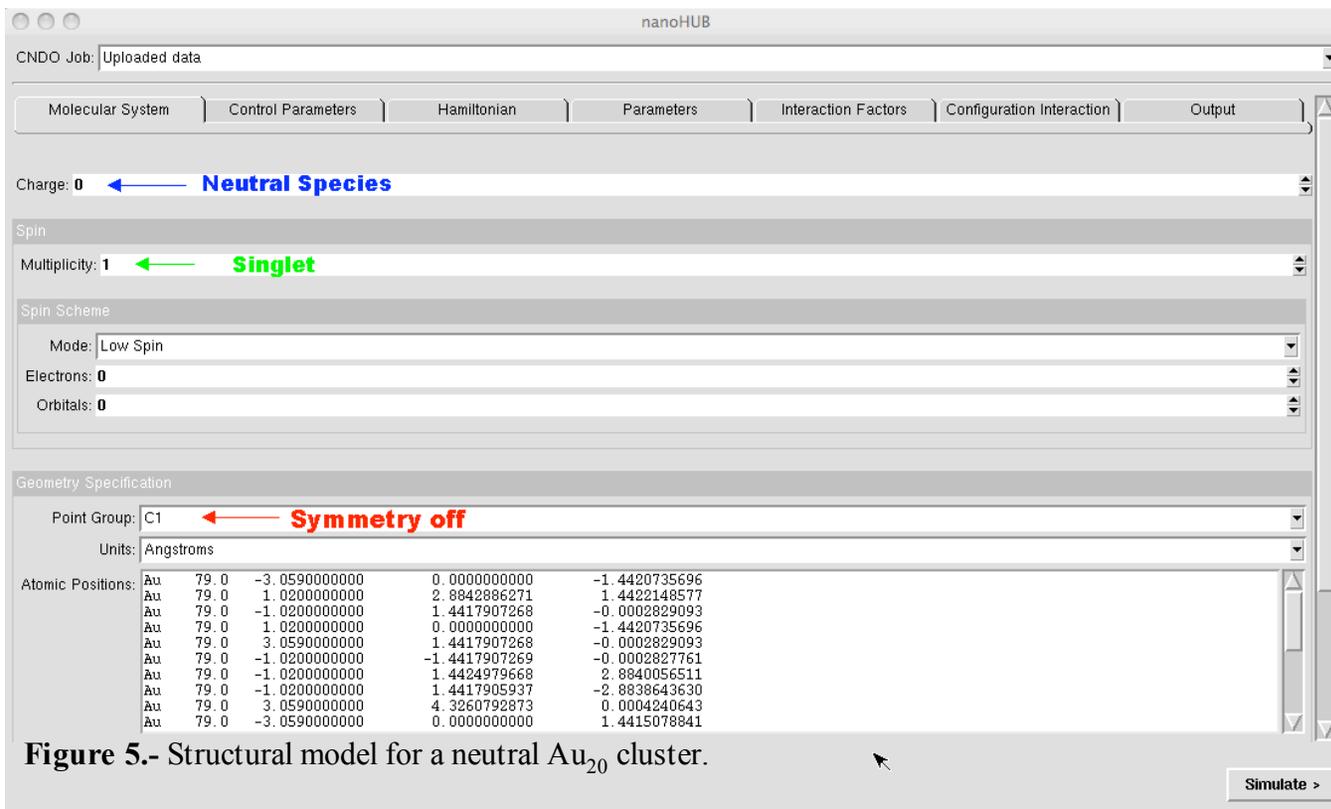


Figure 4.- Defining the chemical model: atomic coordinates, charge and spin multiplicity.

## Molecular geometry, charge and multiplicity

Once the structure has been entered, the electric charge and the spin multiplicity of the system must be specified. Enter the appropriate values for the *Charge* and *Multiplicity*. In the case of the Au<sub>20</sub> cluster we will assume that the particles are neutral (*Charge*=0) and all the electrons are paired with opposite spins.<sup>5</sup>



The screenshot shows the nanoHUB interface for a CANDO job. The 'Charge' is set to 0, labeled 'Neutral Species'. The 'Spin' section shows 'Multiplicity: 1' labeled 'Singlet'. The 'Spin Scheme' is set to 'Low Spin' with 'Electrons: 0' and 'Orbitals: 0'. The 'Geometry Specification' section shows 'Point Group: C1' labeled 'Symmetry off' and 'Units: Angstroms'. Below this is a table of atomic positions for 20 Au atoms.

Atom	X (Å)	Y (Å)	Z (Å)
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	1.0200000000	2.8842886271
Au	79.0	-1.0200000000	1.4417907268
Au	79.0	1.0200000000	0.0000000000
Au	79.0	3.0590000000	1.4417907268
Au	79.0	-1.0200000000	-1.4417907269
Au	79.0	-1.0200000000	1.4424979668
Au	79.0	-1.0200000000	1.4417905937
Au	79.0	3.0590000000	4.3260792873
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000
Au	79.0	-3.0590000000	0.0000000000

**Figure 5.-** Structural model for a neutral Au<sub>20</sub> cluster.

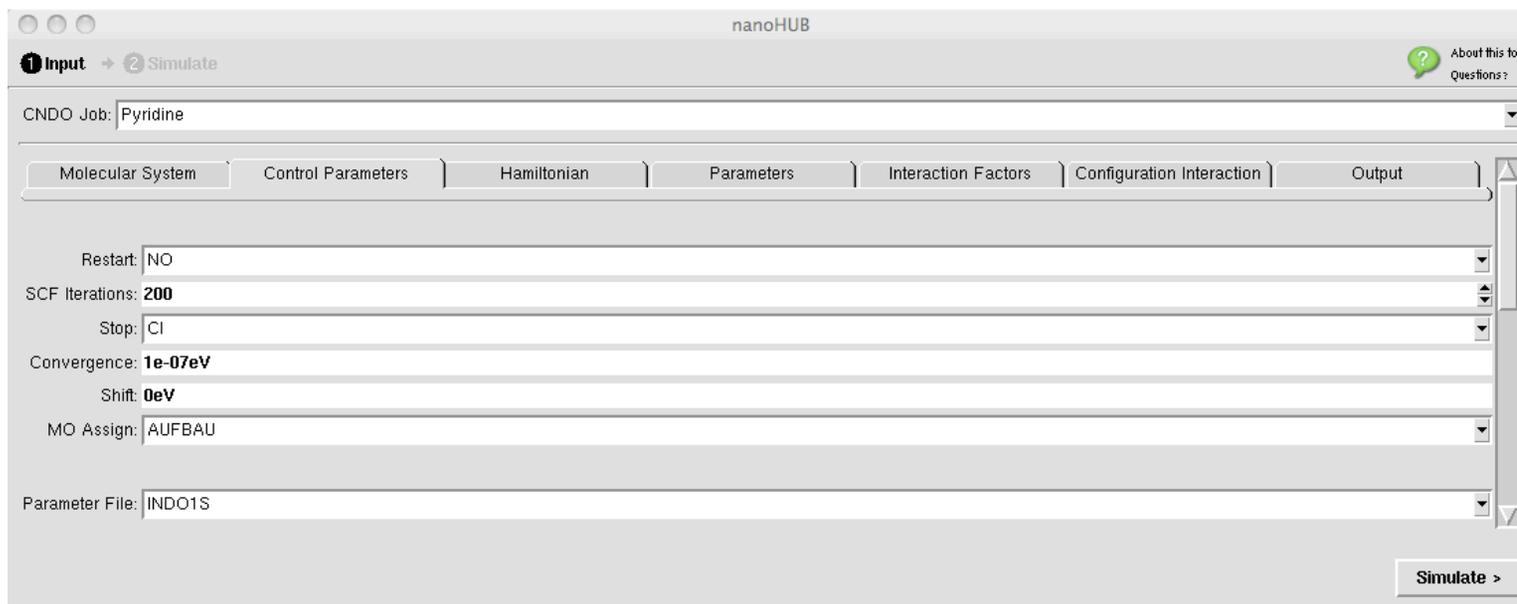
To complete the description of the system, we have to provide the theoretical approach that we will utilize in the computation. In our study we will calculate the wave function by solving the Schrödinger equation using the approximate, semiempirical method INDO (Intermediate Neglect of Differential Overlap).

(5) Remember that the spin multiplicity of a system is defined by the number  $2S+1$  where  $S$  is the sum of the individual electron spins.

## Simulation parameters

### 2c.– *Simulation parameters.*

The Schrödinger equation is solved iteratively using the SCF or Self-Consistent Field method. Figure 6 shows the parameters that control the calculation. In the SCF method, the wave function is recomputed cyclically until the associated energy converges that is, the difference in energy between two consecutive iterations drops below a predefined threshold. The limit is specified by the parameter *Convergence* in the Control Parameters tab. In this exercise, we will use  $10^{-5}$  eV as the energy threshold and 200 *SCF Iterations*. This means that if the energy has not converged in 200 SCF iterations, the program will stop. It is a good practice to keep this parameter small, run the calculation and observe the SCF trend: if in the first few iterations it oscillates, stop the calculation and increase the SCF damping factor (Parameter *Shift* in Control Parameters). Then rerun the calculation. For small systems, the solution is generally found in fewer steps. If the SCF procedure is converging but it needs more iteration steps, it is possible to restart the calculation. See the section **Restarting Computation**.



The screenshot shows the nanoHUB interface for a simulation. At the top, the job name is "Pyridine". Below the job name, there are several tabs: "Molecular System", "Control Parameters", "Hamiltonian", "Parameters", "Interaction Factors", "Configuration Interaction", and "Output". The "Control Parameters" tab is selected. The parameters are as follows:

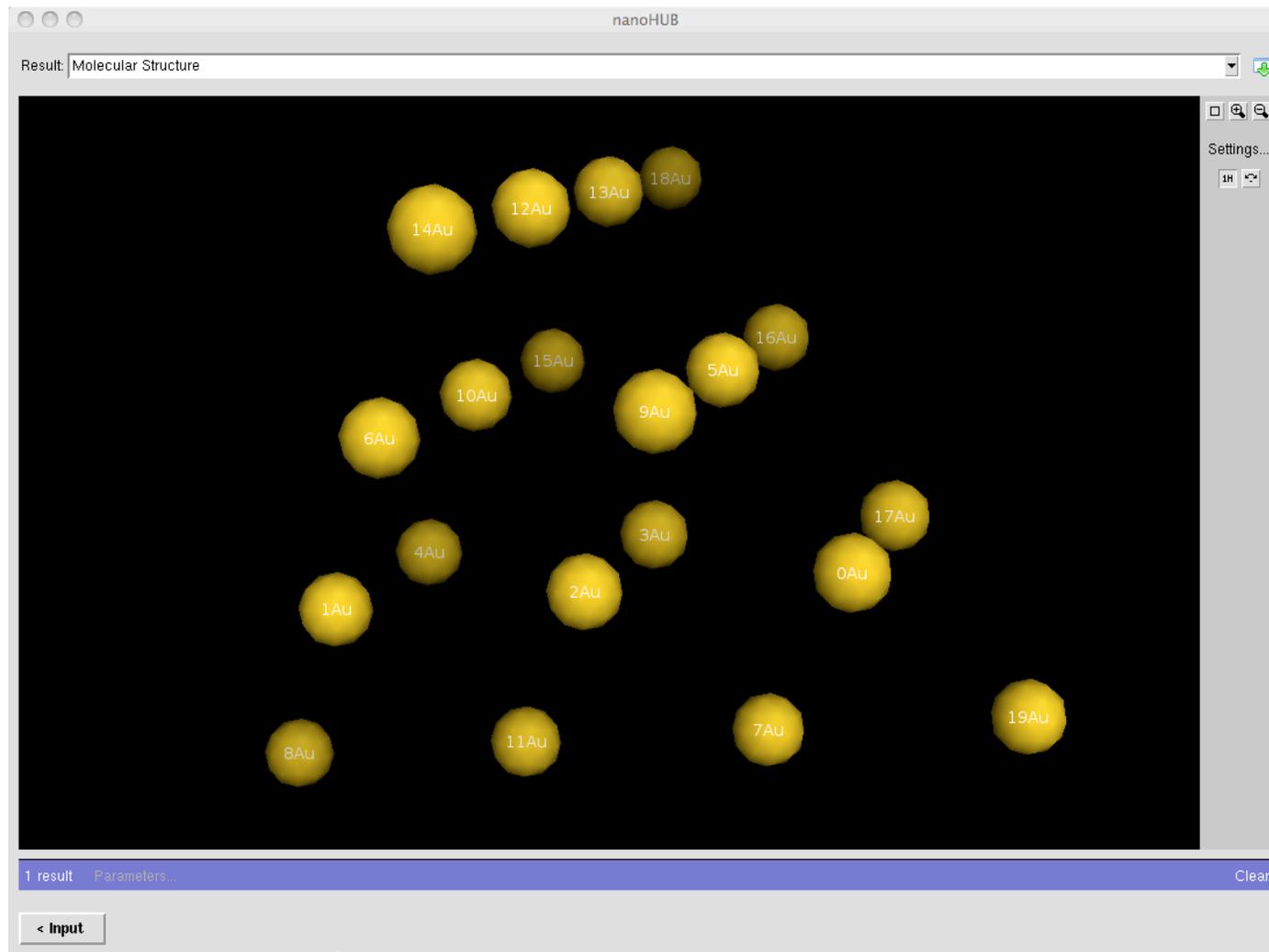
Parameter	Value
Restart	NO
SCF Iterations	200
Stop	CI
Convergence	1e-07eV
Shift	0eV
MO Assign	AUFBAU
Parameter File	INDO1S

A "Simulate >" button is located at the bottom right of the interface.

**Figure 6.-** Simulation Control Parameters. The default values are appropriate for most of the calculations so in general they do not need to be changed.

## Analysis of results

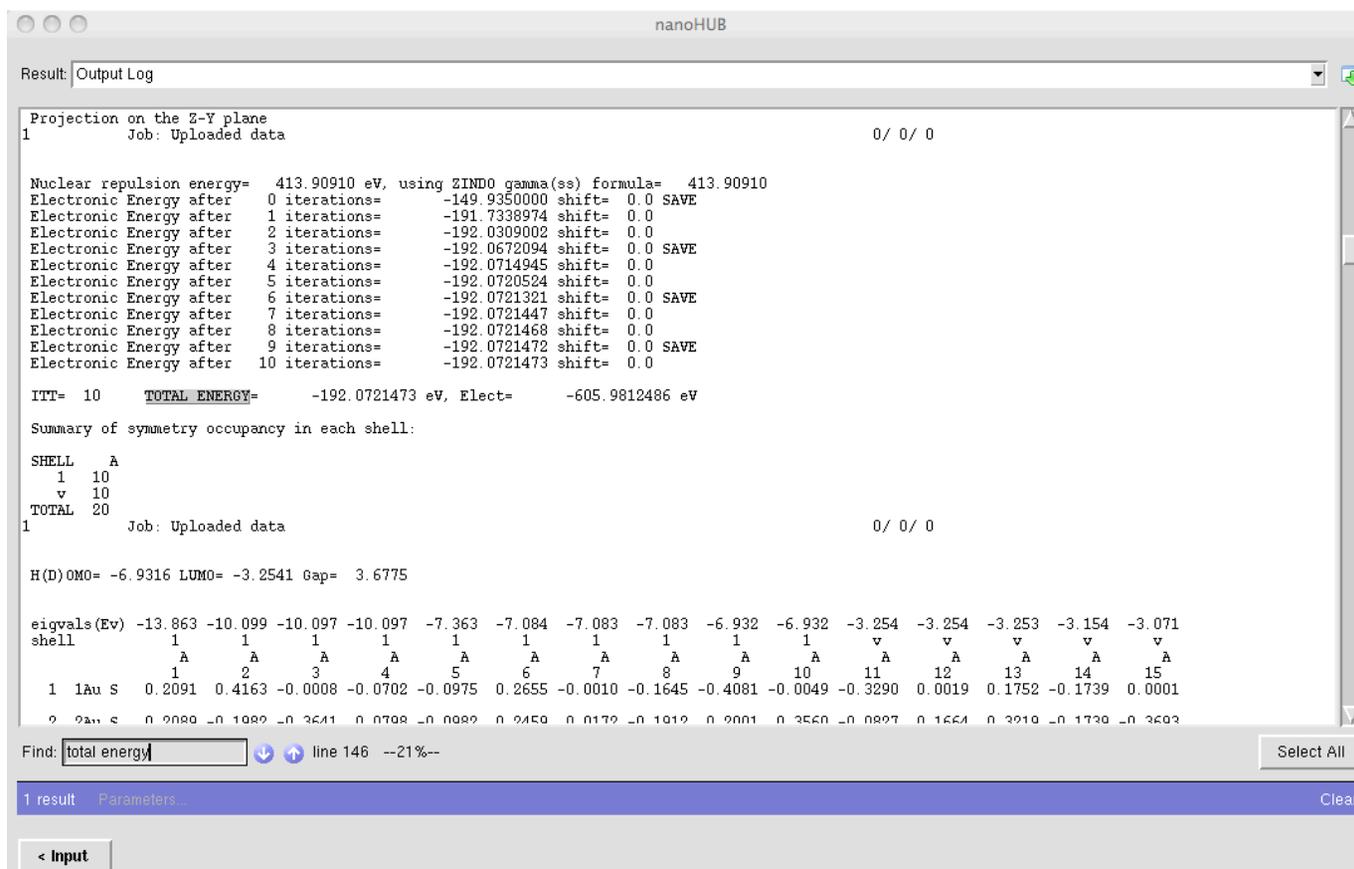
After the computation has finished, a new window will automatically appear showing the picture of the structure (atomic configuration) of the system under study (See Figure 7).



**Figure 7:** Structure of the particle  $\text{Au}_{20}$  showing the atomic labels.

# Total Energy

In order to verify that the calculation has been successfully completed we must make sure that the SCF procedure has converged. On the *Result* menu, select the option Output Log. The window contains the description of the system and the results of the calculation. You may either download its content to your local computer for further reference (advisable), or search for specific information on-line using the built-in 'Find:' button located at the lower part of the window. For instance, search for the text "total energy"; if the string is found, its first appearance will be highlighted (see Figure 8). In the example, the SCF took 10 iterations to find a solution for the semiempirical (INDO) Hartree-Fock equation. The total energy, sum of the electronic and nuclear energies, is  $-192.0721473 \text{ eV}$ . A few lines below it is the energy that separates the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals,  $3.6775 \text{ eV}$ .



The screenshot shows the nanoHUB interface with the 'Output Log' window open. The window title is 'nanoHUB' and the content area displays the following text:

```
Projection on the Z-Y plane
1 Job: Uploaded data 0/ 0/ 0

Nuclear repulsion energy= 413.90910 eV, using ZINDO gamma(ss) formula= 413.90910
Electronic Energy after 0 iterations= -149.9350000 shift= 0.0 SAVE
Electronic Energy after 1 iterations= -191.7338974 shift= 0.0
Electronic Energy after 2 iterations= -192.0309002 shift= 0.0
Electronic Energy after 3 iterations= -192.0672094 shift= 0.0 SAVE
Electronic Energy after 4 iterations= -192.0714945 shift= 0.0
Electronic Energy after 5 iterations= -192.0720524 shift= 0.0
Electronic Energy after 6 iterations= -192.0721321 shift= 0.0 SAVE
Electronic Energy after 7 iterations= -192.0721447 shift= 0.0
Electronic Energy after 8 iterations= -192.0721468 shift= 0.0
Electronic Energy after 9 iterations= -192.0721472 shift= 0.0 SAVE
Electronic Energy after 10 iterations= -192.0721473 shift= 0.0

ITT= 10 TOTAL ENERGY= -192.0721473 eV, Elect= -605.9812486 eV

Summary of symmetry occupancy in each shell:
SHELL A
1 10
v 10
TOTAL 20
1 Job: Uploaded data 0/ 0/ 0

H(D)OMO= -6.9316 LUMO= -3.2541 Gap= 3.6775

eigvals(Ev) -13.863 -10.099 -10.097 -10.097 -7.363 -7.084 -7.083 -7.083 -6.932 -6.932 -3.254 -3.254 -3.253 -3.154 -3.071
shell 1 1 1 1 1 1 1 1 1 1 v v v v v
A A A A A A A A A A A A A A A
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
1 1Au S 0.2091 0.4163 -0.0008 -0.0702 -0.0975 0.2655 -0.0010 -0.1645 -0.4081 -0.0049 -0.3290 0.0019 0.1752 -0.1739 0.0001
2 2Au S 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
```

The 'TOTAL ENERGY' line is highlighted in blue. At the bottom, a search bar contains 'total energy' and the result is shown as 'line 146 --21%--'. There are also 'Select All' and 'Clear' buttons.

**Figure 8** Output Log showing the converged SCF total energy (highlighted) after 10 SCF cycles and the HOMO/LUMO energy gap,  $3.6775 \text{ eV}$ .

## Output: Charge distribution.

The reactivity of a molecule may be inferred from its electron density distribution. One way to quantify such a distribution is by means of a *charge population analysis*. The charge at each atomic center is assigned by the sum of its nuclear charge (atomic number) and the number of electrons occupying the orbitals belonging to that atom. Figure 9 shows the resulting *Orbital Occupancy* of the converged wave function. The gold atoms with occupancy less than 1 in the valence atomic orbital  $6s$  have given up electron density to other atoms of the cluster and hence will bear a positive charge. On the contrary, if the occupancy is more than 1 electron they will be assigned a partial negative charge. The numerical values obtained for the  $\text{Au}_{20}$  system are shown in the column labeled *Charge*, highlighted on Figure 9. In the log file window, the population analysis section may be located by searching for the string charge.

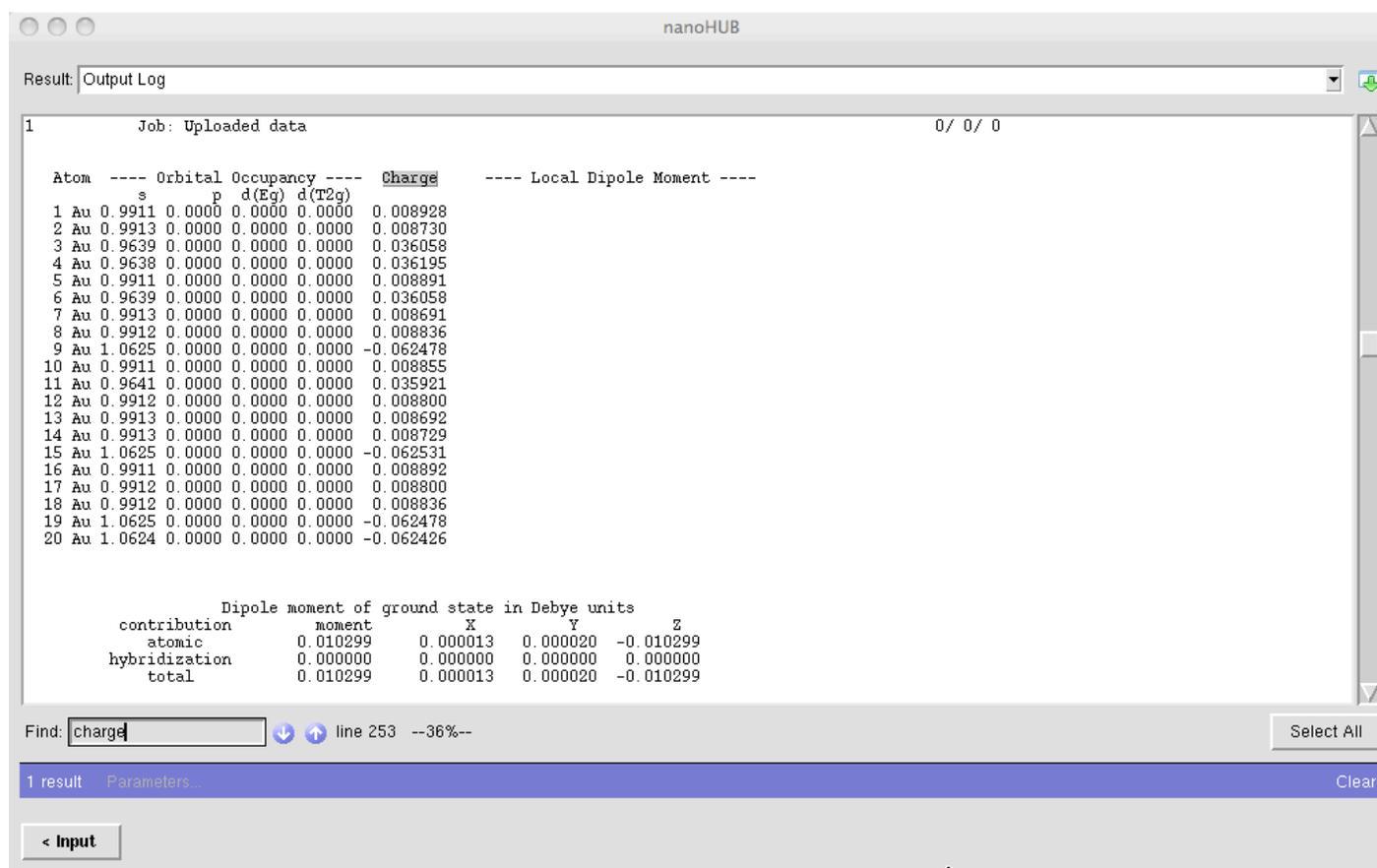
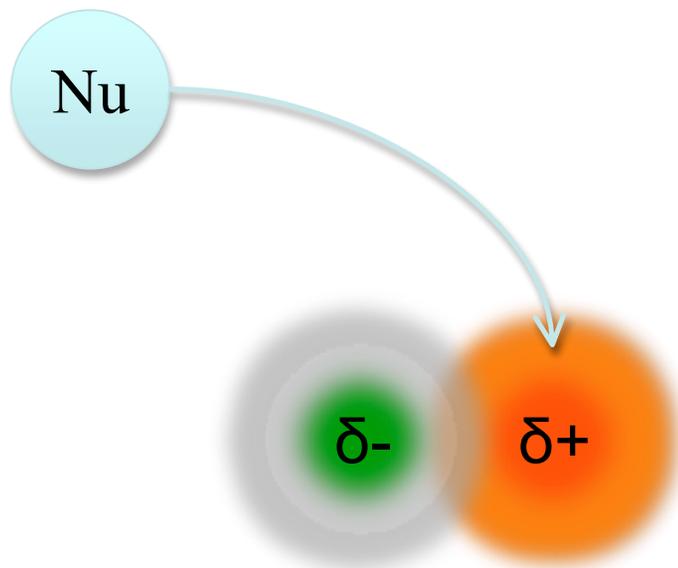


Figure 9: Atomic charge population analysis of the  $\text{Au}_{20}$  particle.

## Output: Charge distribution.

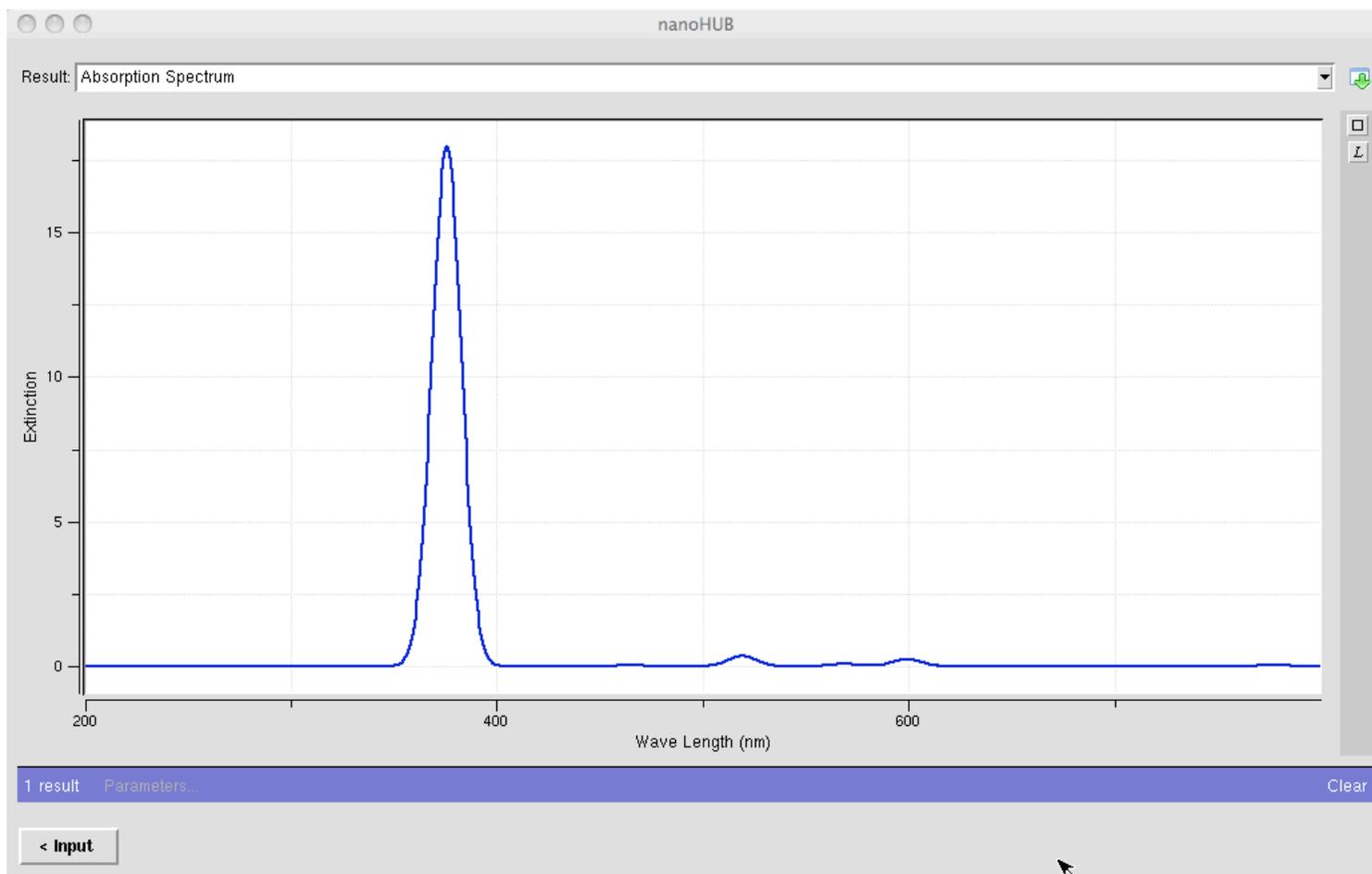
Based on the electron population analysis, we may define an *electrostatic* criterion to predict which centers in the Au<sub>20</sub> will likely react with nucleophilic (e.g., positive Au atoms will attract nucleophilic ligands) species and which will react with electrophilic species. Although these electrostatic interactions may seem to be a reasonable argument to predict the initiating step of a reaction, it may not be sufficient, as *electronic* factors (i.e., which orbitals can combine to form bonds) are also in effect. Indeed electronic factors may dominate in the overall mechanism and change the direction of the reaction predicted by electrostatic factors alone. In a chemical process, the total energy is the factor that determines which product is more stable.



**Figure 10:** The charge distribution on the system may reveal the reactivity sites for nucleophilic and electrophilic species.

## Output: Optical Properties.

The absorption spectrum may be analyzed by reading the log file (search for the string wavelength), or with a tool that provides a graphical representation of this data showing the simulated UV/Vis spectrum as function of the wavelength. On the 'Result' options menu, select "Absorption spectrum". The results obtained for the Au<sub>20</sub> cluster are shown on Figure 11.



**Figure 11:** Calculated absorption spectrum of pyramidal, neutral Au<sub>20</sub> particles.

## Restarting current computation

It is possible that the energy will not converge in the specified number of SCF iterations. In these cases, it is possible to restart and continue the calculation from the end of the previous one. To do so, first locate the SCF steps in the *Output Log* and make sure that the energy shows a convergent trend. Then, click on the *Input* button, which will take you back to the input window, and open the *Control Parameters* dialog tag as shown in Figure 11. On the *Restart* option select YES and for *MO Assign* pick PREVIOUS. At this point, the computation may be restarted by clicking on the *Simulate* button.



**Figure 11:** Restarting incomplete SCF calculations. Set *Restart:* YES and *MO Assign:* PREVIOUS.

## Practice questions and exercises.

The Cartesian coordinates of the structures are available for download on ....??? ([www.nanohub.org](http://www.nanohub.org)) somewhere.

A Nanoparticles (structure comparisons).

1.- Nucleation.

The files [M4 Tetrahedral.xyz](#) and [M4 Planar.xyz](#) (with M= Ag and Au) contain the coordinates for the tetrahedral and planar  $M_4$  clusters, respectively. Using the semiempirical method INDO, calculate the electronic structures and tabulate the total energies of the clusters as a function of the geometry and the nature of the metal M.