

Theoretical Characterization of CdSe Clusters

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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.

I. Introduction

- The physical properties of a molecular system may be approximately calculated from the solution of the Schrödinger equation. The complexity of this solution increases rapidly with the size of the system (number of atoms) so for the CdSe clusters that we study in this project, we resort to semiempirical methods in which the evaluation of computationally expensive parameters is avoided by using values for these parameters that are obtained from experiment.
- In this section, we will learn how to model clusters of CdSe and how to obtain some of its properties using a semiempirical method called INDO “intermediate neglect of differential overlap”.¹
- Having as a reference the data collected in the experimental part of this laboratory, we will be able to assess the quality of the model by comparing the theoretical predictions with experiment. In addition, the correlation between experiment and theory may serve as a guide to making predictions of properties other than those being experimentally measured.

(1) J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (Mcgraw-hill, New York, 1970).

II. Procedure

•All calculations will be carried out using the program CNDO/INDO accessible on-line at the NanoHUB (<http://www.nanohub.org>). A series of CdSe clusters will be considered to establish a correlation between the size of the particle and the optical properties of the material, in a similar manner as we did in the experimental part of the laboratory. The respective files containing the Cartesian coordinates of the clusters are available on the course website (<https://www.nanohub.org>). The geometries of these clusters were obtained from the crystal structure of the cadmoselite (CdSe mineral) experimentally determined by X-Ray diffraction.²

•Log into the NanoHUB and open the page under the link “My nanoHUB”. The group menu “My Tools” lists your favorite tools so that you can quickly access them in later sessions. First, under the tag ‘All Tools’ search for “CNDO/INDO” and click on the star next to it; it will mark the tool as ‘Favorite’ and place it in that folder. This is the general procedure to configure your tools; however, in this particular case you may navigate to the location of the tool through its link <http://www.nanohub.org/tools/endo>. This will take you to the main window of the program; you may read here a brief summary about it and find useful bibliographic references one should use to document the work in which this tool has been employed.

•To access the program, simply click on the highlighted text “Launch Tool” located on the right-hand side of web page. [Figure 1](#) shows the window of the tool with the input section “Molecular System”. The parameters shown correspond to the molecule pyridine which is provided as a demonstration. The topmost menu bar on the window contains several other examples with predefined parameters. If you click on the menu, you will see three options labeled “New”, “Upload” and “Download” which respectively allow you to create a new job, upload data from your local computer to the nanoHUB, or download it. In practice, the second option will be the most commonly used as we will be studying a system whose structural model is provided to you separately as a download from the *NanoHUB*. Each line of the download files contains the atomic symbol of an atom in the cluster, followed by the atomic number and then the position as specified by the three Cartesian coordinates. You may look at the section “Atomic Positions” (under “Geometry Specification”) to see an example of this for pyridine ([Figure 1](#)).

(2) Xu, Y.-N.; Ching, W. Y. *Phys. Rev. B* **1993**, *48*, 4335.

II. Procedure

The screenshot shows the nanoHUB interface for the CNDO/INDO tool. The job name is 'Pyridine'. The interface is divided into several sections:

- Charge:** 0
- Spin:** Multiplicity: 1
- Geometry Specification:**
 - Point Group: Auto
 - Units: Angstroms
 - Atomic Positions:
- Solvent:**
 - Radius: 0.0
 - Dielectric Constant: 78.0
 - Refractive Index: 1.333

The Atomic Positions table is as follows:

Atom	X	Y	Z
N	7.0	0.000000	0.000000
C	6.0	1.212436	0.000000
C	6.0	1.212436	-0.700000
C	6.0	0.000000	-1.400000
C	6.0	-1.212436	-0.700000
C	6.0	-1.212436	0.700000
H	1.0	2.154671	0.000000
H	1.0	2.154671	-1.244000
H	1.0	0.000000	-2.488100
H	1.0	-2.154671	0.000000

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

Figure 1.- The tool CNDO/INDO showing the menu that controls the chemical model parameters for the molecule of pyridine: charge (0), spin multiplicity (1, singlet), geometry (Cartesian coordinates in Angstroms) and solvent specification parameters.

II. Procedure

Let us continue the description with one of our target systems. The simplest model is the cluster $(\text{CdSe})_6$ whose geometry is in the file [Cd6Cd6.xyz](#). Upon download, please make sure that the file is located in an accessible folder on your computer). The next step will be to upload to the INDO program on the NanoHUB.

a) *Uploading the structure*: On the CNDO window, select ‘Upload’ from the “CNDO Job” menu and follow the instructions given on the popup window. Please note that you must have the “pop-up windows” options enabled on your web browser, usually located on the ‘preferences’ menu. You can either import the coordinates file or copy/paste them. In either case, you should see the coordinates with the appropriate format placed on the ‘Atomic Positions’ section of the CNDO “Molecular System” menu.

b) *Selection of the total charge and spin multiplicity*. – The specification of charge and spin multiplicity is crucial in the formulation of the theoretical model. An erroneous input on either one will bring about a system/computer error or even worse, meaningless results. The *charge* determines whether the cluster is an ion or a neutral species while the spin multiplicity indicates how many unpaired electrons there are. This number is $2S + 1$ where S is the overall electron spin. If all the electrons are paired, then the system is “closed shell” and the total spin is zero ($S=0$). As discussed in class, higher spin values can arise if there are unpaired electrons. If the system has an odd number of electrons then the total spin must be a must be $\frac{1}{2}$, $\frac{3}{2}$, etc while an even number of electrons gives rise to $S = 0, 1, 2, \dots$. The spin multiplicity indicates the number of independent states that can occur. Thus for $S = 0, \frac{1}{2}, 1$, etc we have *singlet*, *doublet*, *triplet*, etc. states, respectively.

Q: The CdSe is a diamagnetic material. Assuming that the particles are neutral, determine the spin multiplicity of each CdSe cluster.

Procedure: Selection of the Hamiltonian

c) *Selection of the Hamiltonian.* Once the structure, charge and spin multiplicity have been defined, you should select the Hamiltonian operator (energy function) that will be used to solve the Schrödinger equation. For this, select the tab “Hamiltonian” on the main window of the tool and select INDO (Figure 2). This option will automatically use the appropriate parameters (basis set) for each atom in the structure. These parameters are located in an internal file that is selected in the “Control Parameters” section (see Figure 4). Once the Hamiltonian is defined, the Schrödinger equation for the ground state of the cluster is solved by iteration using a method called the SCF (Self-Consistent Field) method.

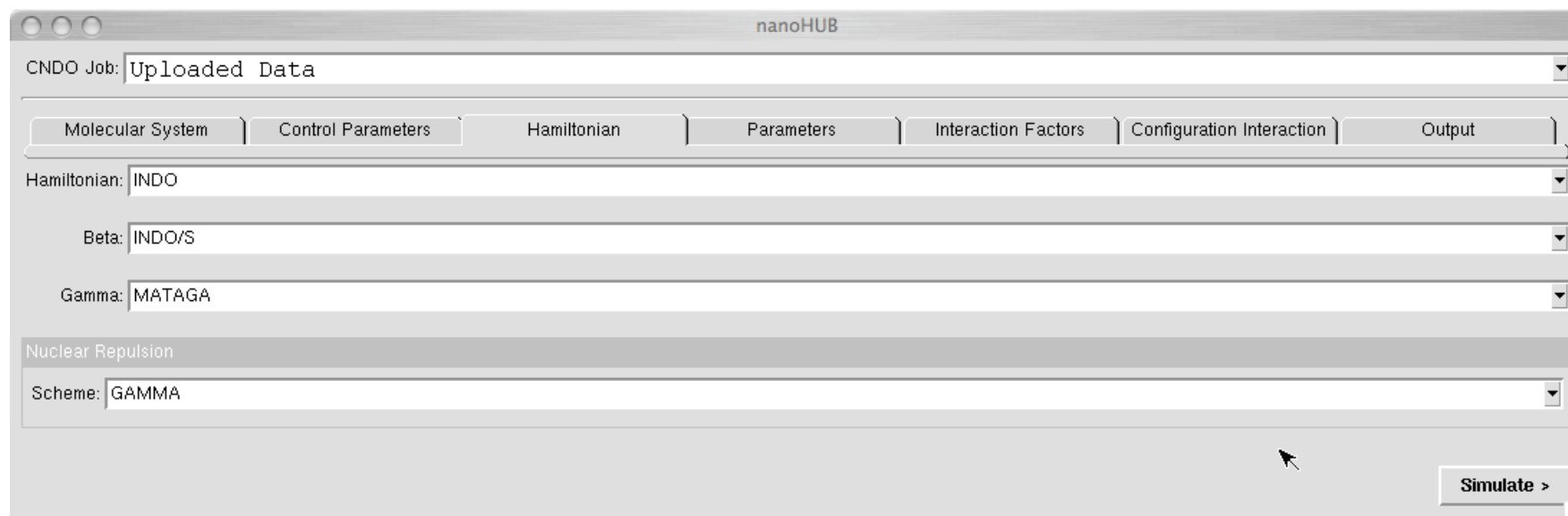


Figure 2: Selection of the Hamiltonian operator.


Procedure: Post-SCF – Configuration Interaction

d) *Post-SCF calculation* (Configuration Interaction - CI). Once the SCF equations have been solved, we need to determine the excited electronic states of the cluster so that its spectrum can be determined. This is done by constructing wavefunctions, here denoted “configurations” that involve exciting electrons from the ground state to various excited states, (See [Figure 3](#)) and then letting these configurations interact with each other (due to electron repulsions). This is called a Configuration Interactions (CI) calculation. Among the possible excitations of the electrons, only those whose spin multiplicity preserves the total spin of the system imposed in section *b*) are used. This is selected by the parameter “Mult_CI” (enter 1 for *singlet*, 2 for *doublet*, 3 for *triplet*, etc.) in the Configuration Interaction control panel (Figure 3).

The menu option “Max_CI” determines the maximum number of configurations allowed in the CI expansion. The default 60 means that the wave function will be a linear combination of 60 configurations. The CI procedure calculates the set of coefficients that makes the energy minimum. The “XCI” pair of number specifies the group of molecular orbitals that will be used to build the CI expansion. The first integer indicates the number of occupied orbitals from which the electrons are going to be taken in the excitation. The second selects the number of the empty orbitals that may be used for the excited electron. You need to specify that all excitations will be considered coming from the first state (set the Ex_From parameter to 1).

The parameters that can be used in Figure 3 are somewhat interdependent; in many cases the program prevents you from entering wrong or inconsistent values. In other cases, it is even able to detect errors and automatically make the appropriate correction. However, after a job is submitted, it is a good practice to watch for messages telling about the progress of the calculation. After the job has finished, there is a report and summary.

Procedure: Cont'd



The screenshot shows the nanoHUB interface for the Configuration Interaction control panel. The window title is "nanoHUB". The "CNDO Job:" dropdown menu is set to "Uploaded Data". A navigation bar at the top contains tabs for "Molecular System", "Control Parameters", "Hamiltonian", "Parameters", "Interaction Factors", "Configuration Interaction", and "Output". The "Configuration Interaction" tab is active. The panel includes the following controls:

- Mult_CI: 1
- Max_CI: 60
- XCI: 12 18
- Ex From: 1
- Fast_CI: yes
- CI Group: no

A "Simulate >" button is located in the bottom right corner.

Figure 3: Configuration Interaction control panel.



The screenshot shows the nanoHUB interface for the Job control parameters. The window title is "nanoHUB". The "CNDO Job:" dropdown menu is set to "Uploaded Data". A navigation bar at the top contains tabs for "Molecular System", "Control Parameters", "Hamiltonian", "Parameters", "Interaction Factors", "Configuration Interaction", and "Output". The "Configuration Interaction" tab is active. The panel includes the following controls:

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

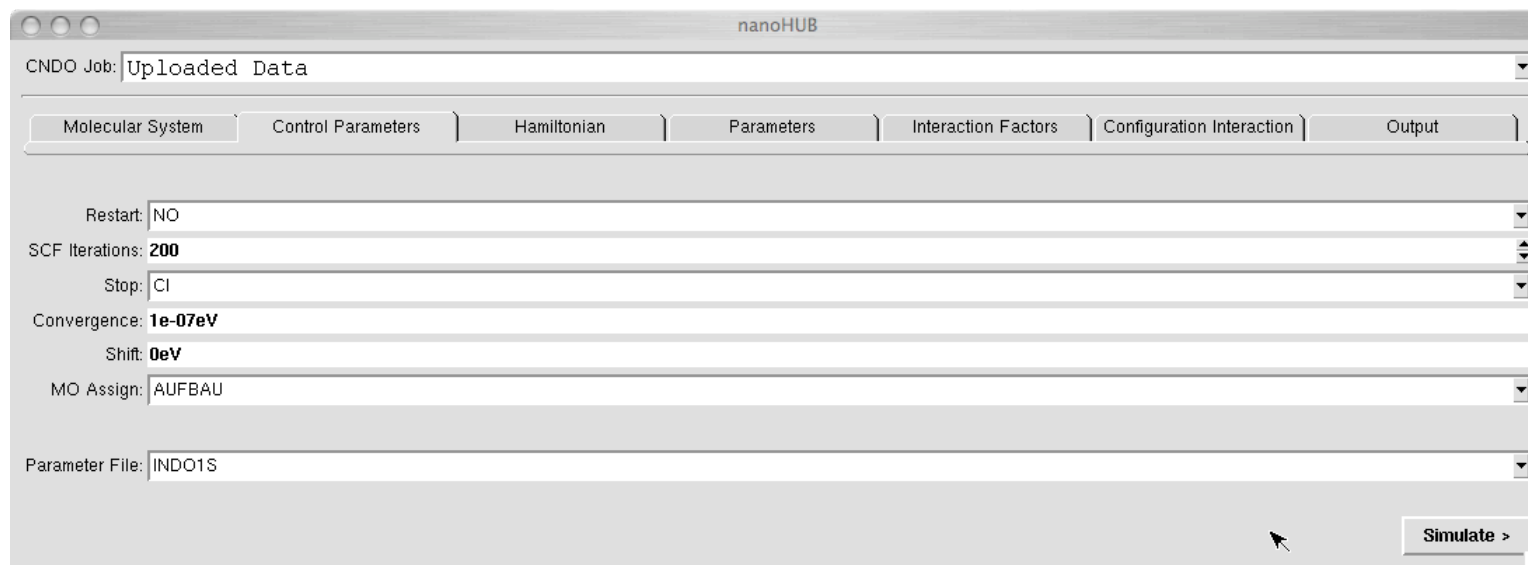
A "Simulate >" button is located in the bottom right corner.

Figure 4: Job control parameters. The default values are appropriate for most of the calculations so in general they do not need to be changed.

Procedure: Control Parameters.

e) *Control Parameters*: These parameters are seldom changed. In special cases, when the default limit of SCF cycles (200) is reached the program stops. However it is possible to restart the calculation by setting the 'Restart' option to either *yes* or *auto*. This is only valid for successive calculations on the same system. In any case a slow energy convergence or even an oscillating sequence of SCF cycles may indicate a bogus model. Before restarting the job, review the input and check for possible errors such with the geometry (coordinates, atomic numbers) and appropriateness of the spin multiplicity and/or charge of the system. These are common sources of problems.

At this point, the chemical model and the theoretical methods to describe it have been defined and the calculation is ready to go. To start click the "Simulate" button on the lower-right corner of the window. In general, for moderately large systems the calculation does not take longer than 10 minutes.



The screenshot shows a web-based interface for nanoHUB. At the top, the title bar reads "nanoHUB". Below it, a dropdown menu shows "CNDO Job: Uploaded Data". A horizontal navigation bar contains several tabs: "Molecular System", "Control Parameters", "Hamiltonian", "Parameters", "Interaction Factors", "Configuration Interaction", and "Output". The "Control Parameters" tab is currently selected. The main area contains several input fields and dropdown menus:

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

In the bottom right corner, there is a "Simulate >" button.

Figure 4: Job control parameters. The default values are appropriate for most of the calculations so in general they do not need to be changed.

III- Analysis of the calculation results

The course of the calculation may be visualized as the main program returns part of the output to the GUI. The calculation will have finished when a picture of the structure appears on the screen. However, we should make sure that the calculation has been successfully finished. For example the total energy of the system should have converged to a constant value during the SCF iterations: Under the menu “Results” select the log file and search for “Energy” using the built-in search utility. Once you have located that string, make sure that the SCF iterations have finished and the electronic energy has converged. If this is the case, the ground state solution to the Schrödinger equation has been found and the wave function may be analyzed for other observables.

1.- Molecular Structure and MO Energy diagram.

1.- *Molecular Structure and MO Energy diagram.* Figure 5 shows a picture of the molecular geometry of the model (pyridine in the example) and, on the right hand side, the diagram of MOs with labels that identify the HOMO and LUMO and the energy gap in eV . The box with the inverted arrow on the top-right side of the window allows downloading the images to your local computer. The buttons underneath are control visualization parameters for the respective images.

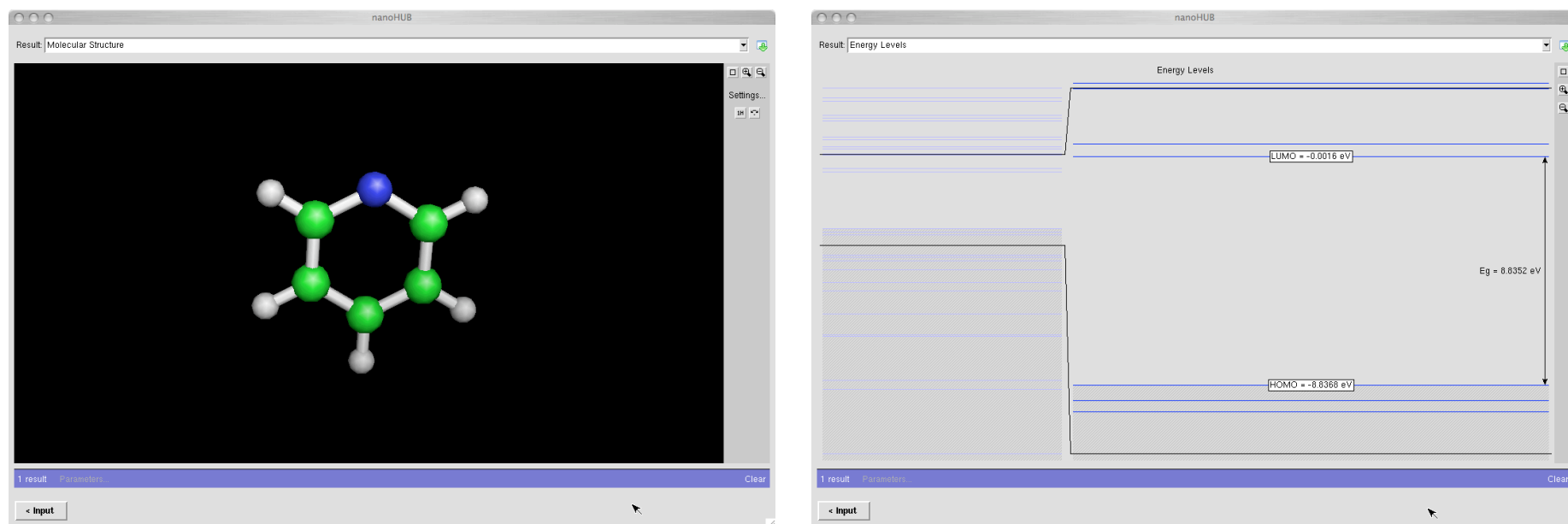


Figure 5: Representation of the molecular structure and the energy diagram of molecular orbitals.

2.- Absorption Spectrum.

2.- *Absorption Spectrum*. By selecting the appropriate option on the “Results” menu, you can visualize the theoretical UV/Vis absorption spectrum. Figure 6 shows the spectrum of pyridine in the range 200 to 800 nm. By clicking on the axis of coordinates (X or Y), you can select the desired range as shown on the picture on the right. The square buttons on the upper right hand side of the spectrum permits resetting the view or selecting/unselecting specific curves when multiple values are plotted on the same graph. It is possible to download the plot either as an image or raw data. Use the *download* button for this purpose. The values (X, Y) of a specific point may be displayed by placing the mouse pointer on top of the curve at the desired point. Of special importance is the value of wavelength at which the substance shows peak absorption (λ_{\max}).

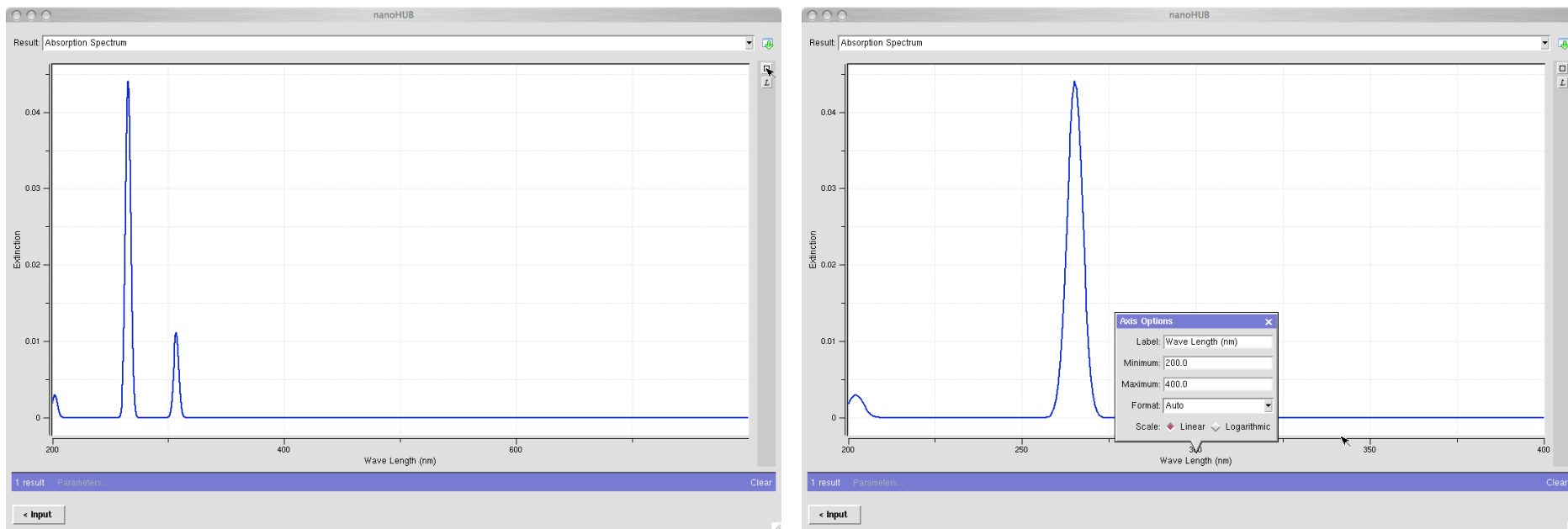


Figure 6: Calculated absorption spectrum of the molecule of pyridine. A section of the spectrum between 200 and 400nm is shown on the right.

3.- The Log files.

4.- *Log files.* All the information that the program represents graphically is recorded in a log file. You may search this for specific numerical values (energies, dipole moments, basis functions coefficients, etc.). This is available in the “Output log” of the “Results:” menu. To facilitate searching this file, use the *Find* text button at the bottom of the window as illustrated in Figure 7. In this example, the string “total energy” is searched. The total energy of the system (nuclear repulsion plus electronic energy) is given in eV . On the same line, we can see the number of iterations (SCF cycles) that the program needed to solve the Schrödinger equation. Next follows a brief summary of the number and class of MOs, labeled according to their symmetry, the HOMO-LUMO energy gap, and then a long list of the orbitals, preceded by their corresponding orbital energies.

IMPORTANT: If the SCF iterations do not converge the rest of the output is bunkum and must be disregarded. The causes must be analyzed and fixed: *i)* verify the input geometry and atomic configuration - coordinates (does the model make sense?) *ii)* review the charge and spin multiplicity.

If the SCF is converged, the CI calculation will be done. This output is shown in Figure 8; you can search for the string “ci excitations” to visualize that section of the log file.

After the CI equation is built, the program optimizes the coefficients to find an energy minimum. The ground state energy is then taken to be zero, and the excitation energies are determined relative to this. Figure 9 shows the part of the log file in which you can read these parameters. The Jablonski diagram may be calculated from these energy values.

3.- The Log files.

```
nanoHUB
Result: Output Log
Electronic Energy after 18 iterations= -1075.0334838 shift= 0.0 SAVE
Electronic Energy after 19 iterations= -1075.0334889 shift= 0.0
Electronic Energy after 20 iterations= -1075.0334916 shift= 0.0
Electronic Energy after 21 iterations= -1075.0334932 shift= 0.0 SAVE
Electronic Energy after 22 iterations= -1075.0334941 shift= 0.0
Electronic Energy after 23 iterations= -1075.0334946 shift= 0.0
Electronic Energy after 24 iterations= -1075.0334948 shift= 0.0 SAVE
Electronic Energy after 25 iterations= -1075.0334950 shift= 0.0
Electronic Energy after 26 iterations= -1075.0334951 shift= 0.0

ITT= 26 TOTAL ENERGY= -1075.0334951 eV, Elect= -2751.2645564 eV

Summary of symmetry occupancy in each shell:

SHELL A1 A2 B1 B2
1 7 1 2 5
v 6 1 2 5
TOTAL 13 2 4 10
1 Job: Pyridine 0/ 0/ 0

H(D)OMO= -8.8368 LUMO= -0.0016 Gap= 8.8352

eigvals(Ev) -44.070 -33.984 -32.557 -25.673 -25.443 -22.267 -18.561 -17.290 -15.284 -13.934 -13.376 -13.034 -9.872 -9.425 -8.837
shell 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
A1 A1 B2 A1 B2 A1 B2 A1 B2 A1 B1 A2 A1 B1 A2
1 1 N S 0.4543 -0.5027 0.0000 -0.2908 0.0000 -0.2182 0.0000 0.2314 0.0000 -0.1352 0.0000 0.0000 0.3747 0.0000 0.0000
2 1 N Px 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 -0.4767 0.0000 0.0000 -0.6123 0.0000
3 1 N Py 0.0000 0.0000 0.2087 0.0000 -0.4110 0.0000 -0.4651 0.0000 -0.1419 0.0000 0.0000 0.2728 0.0000 0.0000 0.0000
4 1 N Pz -0.1819 0.0793 0.0000 0.0382 0.0000 -0.2117 0.0000 0.0046 0.0000 -0.2998 0.0000 0.0000 0.7378 0.0000 0.0000

5 2 C S 0.3702 -0.1636 0.4142 0.2430 -0.3076 -0.0708 0.0388 -0.1862 -0.0690 0.0852 0.0000 -0.0339 -0.0764 0.0000 0.0000
6 2 C Px 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 -0.4091 0.0000 0.0000 -0.2117 0.4938
7 2 C Py -0.1679 0.1344 0.0516 0.2717 0.0316 -0.1905 0.2891 -0.2216 0.2738 -0.1434 0.0000 -0.2510 0.1082 0.0000 0.0000
8 2 C Pz -0.0495 -0.1864 -0.0915 -0.1664 -0.2342 -0.2692 -0.2854 -0.0602 0.3142 -0.2029 0.0000 -0.0150 -0.2543 0.0000 0.0000

9 3 C S 0.3279 0.2978 0.4177 0.1763 0.2938 0.0340 -0.0426 0.1844 -0.0828 -0.0714 0.0000 0.0042 0.0524 0.0000 0.0000
10 3 C Px 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 -0.3845 0.0000 0.0000 0.3257 0.5062
11 3 C Pv -0.1268 -0.0879 0.0596 0.2460 0.0199 -0.2249 0.1763 0.3020 0.2055 0.1451 0.0000 0.3884 -0.0275 0.0000 0.0000

Find: total energy line 167 --23%-- Select All
1 result Parameters Clear
< Input
```

Figure 7: Section of the *Output Log* file showing the total and electronic energies (in eV) after a successful, 26-iteration SCF calculation.

3.- The Log files.

```
10 H 0.9792 0.0000 0.0000 0.0000 0.020841
11 H 0.9535 0.0000 0.0000 0.0000 0.046502

          Dipole moment of ground state in Debye units
      contribution      moment      X      Y      Z
      atomic           1.435980    0.000000  0.000000 -1.435980
      hybridization    1.482201    0.000000  0.000000 -1.482201
      total            2.918181    0.000000  0.000000 -2.918181

The point group of the molecule is C2V

GAMMA TRANSF  A1= 19 A2= 0 B1= 0 B2= 10
fast_ci= T default_ci= T
Reference determinate nber 1 is ALPHA 1 - 15
Reference determinate nber 1 is BETA 1 - 15
SINGLE excitations FROM orbs 3 to 15 INTO orbs 16 to 29

CI excitations= 60:      A1= 14      A2= 17      B1= 19      B2= 10
CI excitations= 60:      A1= 14      A2= 17      B1= 19      B2= 10
1 Job: Pyridine 0/ 0/ 0

The lowest 60 spin-adapted configurations of multiplicity= 1
sym eV cm**+1 -dets- dipole oscillator X ... Excitations named from first reference determinate
tot # Debye strength

1 A1 0.000 0. 1 1 2.9182 0.000000 0 ( )->( )
2 A1 6.594 53187. 1 1 3.0847 0.565050 1 ( 15)->( 17 )
3 A1 6.762 54536. 1 1 3.1692 0.597441 1 ( 14)->( 16 )
4 A1 8.410 67831. 1 1 2.1612 0.000134 1 ( 14)->( 18 )
5 A1 8.623 69551. 1 1 5.7116 0.042123 1 ( 13)->( 19 )
6 A1 9.304 75041. 1 1 2.1634 0.000088 1 ( 13)->( 21 )
7 A1 9.850 79445. 1 1 2.4029 0.001303 1 ( 11)->( 16 )
8 A1 11.300 91142. 1 1 9.7001 0.037315 1 ( 13)->( 22 )
9 A1 12.149 97992. 1 1 1.3949 0.000201 1 ( 11)->( 18 )
10 A1 12.539 101134. 1 1 4.7827 0.000153 1 ( 12)->( 20 )
11 A1 12.622 101800. 1 1 4.0823 0.071986 1 ( 10)->( 19 )
12 A1 12.797 103213. 1 1 0.7758 0.002106 1 ( 13)->( 24 )
```

Find: line 305 --41%-- Select All

1 result Parameters... Clear

< Input

Figure 8: Output from configuration interaction calculation.

3.- The Log files.

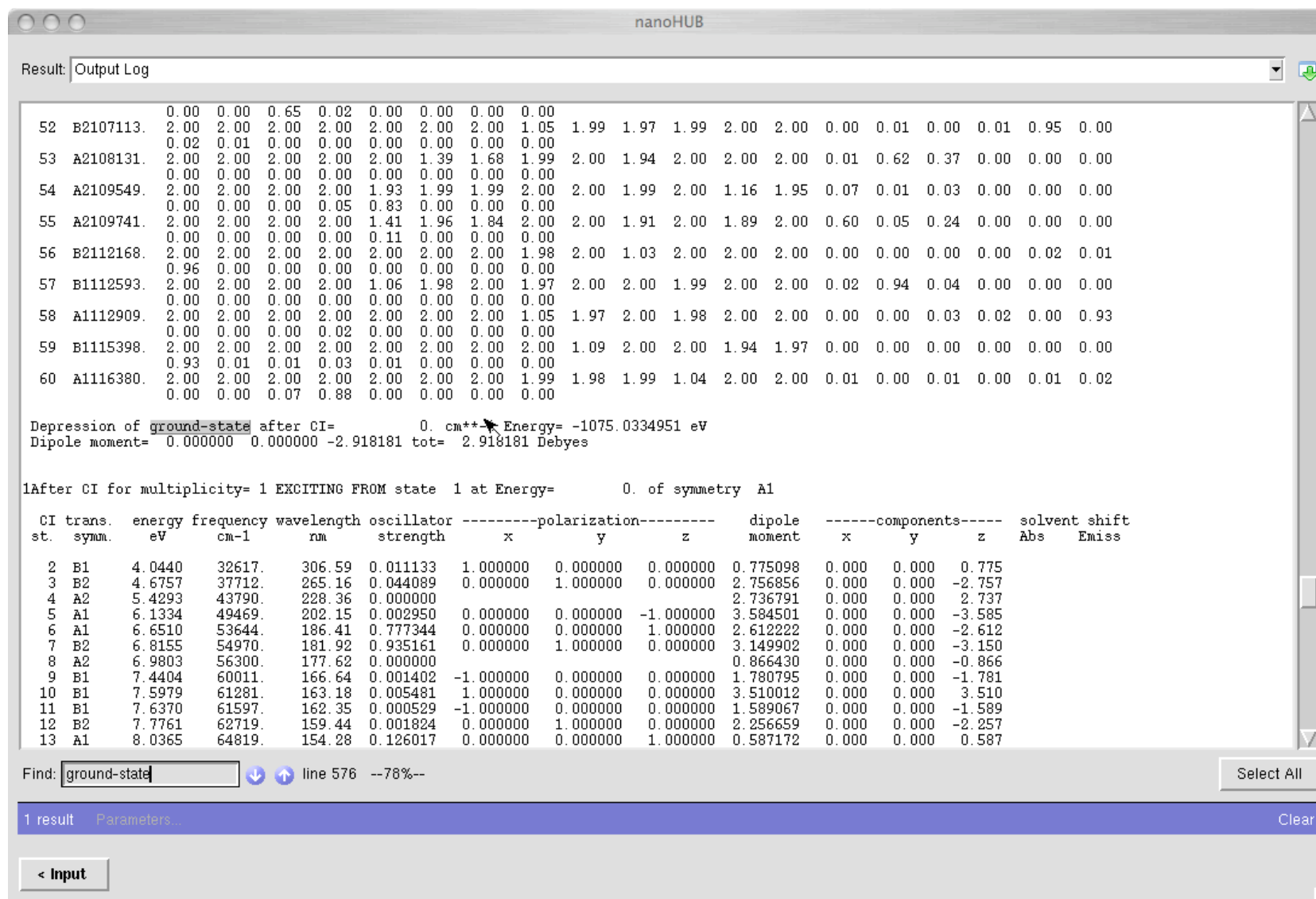


Figure 9: Output showing the electronic states and energies. The strength of the transition (transition dipole moment) is related to the light absorbance by the material; these data is used to plot the UV/Vis spectrum in Figure 6.

4.- Proposed study structures

The files containing the geometry of 5 clusters of CdSe have been deposited in [nanoHUB](#). Their names are labeled according to their stoichiometry $\text{Se}_n\text{Cd}_n.\text{xyz}$, with $n = 3, 15, 30, 55, 176$. shows an example of the structure of the cluster $(\text{CdSe})_{30}$ corresponding to the file Cd30Se30.xyz . Note that these structures were derived from the crystal structure of bulk CdSe, so it is an assumption that these structures are appropriate to describe the nanoparticles in this project.

Download the files to your computer and calculate the electronic structure of each cluster using the program CNDO, as described in the previous sections. Upon completion of the calculations, save the *Output log* files and the graphics (e.g., energy levels, spectra) for further reference as you will need to use these results in reporting your observations and conclusions.

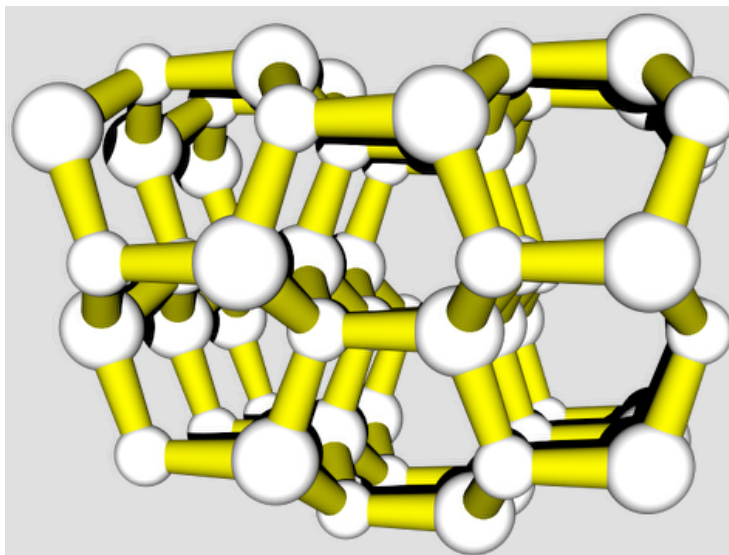
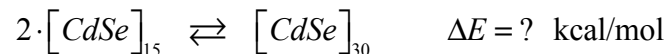


Figure 10: Structure of $(\text{CdSe})_{30}$. This picture has been created using the program [MolST](#) also available on the NanoHUB.

4.- Questions and exercises.

1.- Write the chemical equations that express the formation of the particles and determine the energy involved in the process.



$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

What conclusion may be withdrawn about the stability of the species?

2. Consider the hypothetical cluster $Cd_{29}Se_{30}$. What might be the multiplicity of this cluster? And its charge? Study how these parameters change for the cluster $Cd_{30}Se_{29}$.

3. From the information in the *Output log* files make a Jablonski diagram for the three lowest energy levels for each cluster. (See the sections shown in Figure 9 to determine energy levels).

4.- Plot the absorption spectra and report the λ_{max} value obtained for each clusters. With these data, plot λ_{max} versus size of the cluster (number of atoms). Do these results correlate with the observations carried out in the experiments?

4.- Questions and exercises.

5.- The file [Cd15Se15b.xyz](#) corresponds to a cluster with the same composition as the one studied previously but a different structure. Does the shape of the CdSe particles have any effect on the optical properties of the material?

6.- Suppose that during the synthesis of the CdSe particles, the solution was accidentally contaminated with traces of a soluble Ti(IV) salt. Some of the CdSe particles grew so that a site in the crystal lattice was replaced by Ti. If the cluster $(\text{CdSe})_{24}$ has one site occupied by Ti:

- What would the structure likely be? $\text{Cd}_{24}\text{Se}_{23}\text{Ti}$ or $\text{Cd}_{23}\text{Se}_{24}\text{Ti}$.
- Determine the charge and spin multiplicity of the clusters.
- Analyze the effect of the dopant metal in the nanoparticle.