Synthesis and Size Dependent Properties of CdSe Quantum Dots

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The emerging field of nanotechnology deals with materials that have at least one spatial dimension in the nanometer scale (1-1000nm). Nanomaterials with size dependent properties can be three-dimensional (3-D) colloids, 2-D sheets, 1-D wires, and even 0-D quantum dots.[1] The term quantum dot describes a nanocrystal that is small enough (few nm) that it confines the wavefunction of the excited electron. Quantum dots, also called nanoclusters or nanocrystals, are a perfect example of the quantum mechanical "particle in a box" where the energy of a particle (delocalized electron) decreases as the size of the box (quantum dot) increases.[2] CdSe quantum dots are semiconductors with a band-gap energy, and color, that is dependent on the size of the crystal. This makes them a great material for use in chemical and biological sensors, high-density optical memory, and LED flat panel displays.
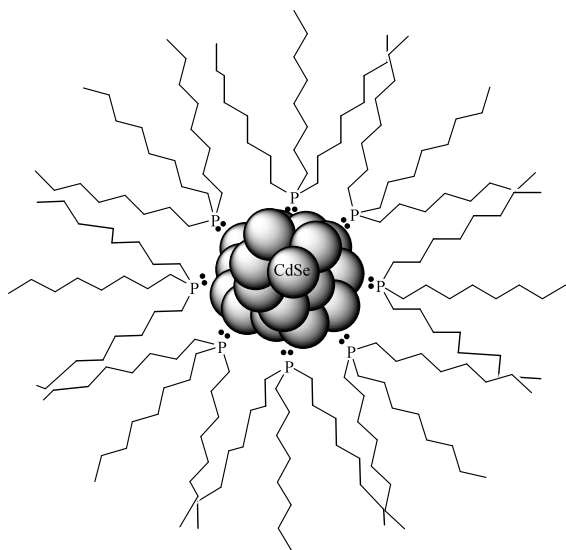

Figure 1 - Graphical representation of a capped CdSe nanocluster.

Capped nanoclusters, such as CdSe quantum dots, consist of small clusters of CdSe in a crystal lattice capped by some ligand. When using trioctylphosphine (TOP) as the capping ligand, the lone pairs of the phosphorus coordinate with Cd^{2+}, creating an organic layer around the nanocluster.[3] The alkyl moeties of the TOP ligand also help to dissolve the quantum dots in organic solvents (Figure 1). The nanocrystals have the same wurtzite structure as bulk CdSe but their size gives them unique properties not seen in the bulk material.[3] By the synthetic procedure using CdO as the precursor, the size of the cluster is controlled kinetically.[4] CdSe aggregates as the reaction proceeds at high temperature and the quantum dots grow larger. Removing aliquots of reaction mixture from the heat quenches this growth yielding quantum dots that are monodisperse in size.
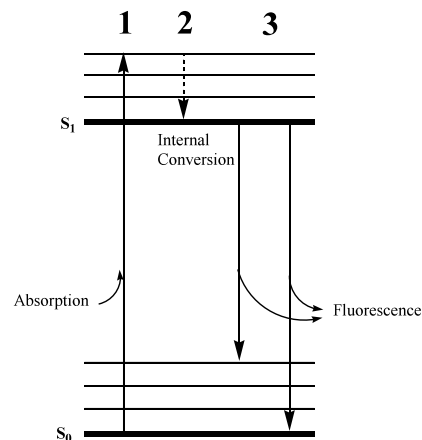
CdSe quantum dots have strong fluorescence in the visible region. Fluorescence is the emission of a photon from a molecule as an electron goes from an excited state to a ground state. The color of the emission depends on the energy difference between states. Electronic absorption and emission processes are summarized in a Jablonski diagram (Figure 2).[5] A photon is absorbed (**1**), exciting an electron from the ground state (S_0) to the first excited state (S_1). The electron relaxes to the lowest vibrational level of the excited state in a process called internal conversion (**2**). Further relaxation to the ground state is accompanied by the emission of a photon as fluorescence (**3**). Fluorescence in quantum dots can be seen with the naked eye following irradiation with UV light (~400nm).

Cadmium is highly toxic because it disrupts zinc-binding proteins in the body. Because of this toxicity, a review of MSDS information for all reagents should be completed and summarized in your lab notebook before lab.

Figure 2 - Jablonski diagram

Procedure:[6]

Se stock solution is prepared by dissolving Se beads in 1-octadecene with trioctylphosphine. It takes ~3hrs at high temperature for the Se beads to dissolve so the stock solution has been prepared for you ahead of time.

1) To a 25mL roundbottom flask, add a magnetic stir bar and 13mg CdO (CdO should be pre-packaged in 13mg portions). **Roundbottom flasks are not disposable; you must wash and return the roundbottom flask.**

2) Add 0.6mL oleic acid and 10mL 1-octadecene to the roundbottom. Since oleic acid is stored at $-20^{\circ}C$, it may be necessary to thaw before use.

3) Clamp the roundbottom flask into the metal heating mantle on the hot plate. Place a thermometer into the heating mantle. **Do not allow the thermometer to heat up beyond the maximum temperature reading (~$250^{0}C$).**

4) Turn on the heat and magnetic stirring.

5) Put aside 10-15 disposable glass vials and two glass pipets with bulbs for the aliquot removal process. When the Se stock solution is added, aliquots must be removed every 30 seconds.

6) Monitor the reaction mixture carefully and add 1mL Se stock solution when all of the CdO has dissolved (solution should be clear to pale yellow).

7) Remove aliquots (~1mL) every 30 seconds with the glass pipets. **Glass pipets will become very hot, handle with care.** Continue collection for about three minutes or until the solution no longer changes color.

8) Turn off heat and remove the roundbottom flask from the heating mantle. **If the flask is allowed to cool while on the heating mantle, it will break.**

9) Irradiate the quantum dot solutions with UV light and make observations.

10) Collect a UV-visible absorption spectrum for one of your quantum dot solutions (assigned by your T.A.). Using data from the class, graph UV-vis spectra and tabulate λ_{max} for all the different colored quantum dots.

Exercises:

1) How many sample aliquots were collected and how did their colors change with increasing reaction time?

2) Which sample contains the smallest quantum dots? Which were the largest?

3) What color light is absorbed (λ_{max}) by the different quantum dot solutions? Comment on the relationship between the observed color and λ_{max} for the different quantum dot solutions.

4) Using the UV-vis data to support your argument, explain how the energy of a delocalized electron changes as the size of the quantum dot increases.

5) Fluorescence (λ_{em}) is shifted to a longer wavelength than the absorption (λ_{max}) for any given fluorophore. This is called the Stokes shift. When the quantum dot solutions were irradiated with UV light, what color emission was observed? Use the Jablonski diagram in Figure 2 to explain why the Stokes shift occurs. (**Hint:** Both ground and excited states have multiple vibrational energy levels.)

1) Alivisatos, A.P. *Science*, **1996**, 271, 933-937
2) See computational section
3) Ozin, G.A.; Arsenault, A.C.; Nanocluster Self Assembly, *Nanochemistry*, Cambridge: RSC Publishing, **2005**; 265
4) Peng, Z.A.; Peng, X. *J. Am. Chem. Soc.*, **2001**, 123,183-184
5)Lackowitz, J.R.; *Principles of Fluorescence Spectroscopy*, 3rd edition, New York: Springer Science, **2006**.
6) Boatman, E.M.; Lisensky, G.C.; Nordell, K.J. *J. Chem. Ed.* **2005**, 82, 11, 1697-1699.

Theoretical Characterization of CdSe Clusters

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I. Introduction

The physical properties (observables) of a molecular system may be approximately calculated from the solution of the Schrodinger equation. Within the Hartree-Fock-Roothaan-Hall formulation,[1] the complexity of the equations increases with the size of the system (No. of atoms) and hence, their *ab-initio* solution quickly becomes a colossal mathematical task limited by the computational resources available in the laboratory. To overcome this technical problem, we resort to approximate (semiempirical) methods which avoid evaluation of certain, usually computationally expensive, parameters by substituting them by a value obtained from experiment, generally spectroscopically.

In this section, we will learn how to model clusters of (CdSe) and how to obtain some of its properties using a theoretical method. Because of the relatively large size of particles that we will study an approximate method will be necessary. In particular, we will use the semiempirical method called INDO "intermediate neglect of differential overlap" {J. Pople, 1967}. Having as reference the data collected in the experimental part of this laboratory, we will be able to assess the quality of the model by contrasting those observations with the theoretical calculations. Even more, we should be able to withdraw conclusions that would have been difficult to measure experimentally. Finally, the correlation between experiment and theory may serve as guide to make predictions on the nature of the system and its properties others than those being experimentally measured.

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 consider 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 at the class blackboard (https:/courses.nothwestern.edu). 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. Firs, 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

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[1] The Hartree-Fock-Roothann-Hall method is based on the Hartree-Fock approximation to solve the Schrodinger equation. It transforms the differential equation into an algebraic system soluble by the SCF procedure.

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

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/cndo. It 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, for instance in this laboratory or in your own research simulations. To call the program, simply click on the highlighted text "Launch Tool" located on the right-hand side of web page. The Figure 1 shows the window of the tool with the input section "Molecular System". The parameters shown correspond to the molecule of pyridine as provided as demonstration example. 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 are usually interested in studying a system whose model has been obtained by a different means. For instance, the files of CdSe clusters you have downloaded from the *blackboard*. The files contain the atomic positions in rectangular Cartesian coordinates with the following format or syntax. Each record of the file contains the specification of one atom of the cluster or molecule. In general, this specification comprises five parameters: First, the atomic symbol, followed by the atomic number and then the position in the space given by the three Cartesian coordinates. You may look at the section "Atomic Positions" (group "Geometry Specification") of the example of pyridine shown in Figure 1.
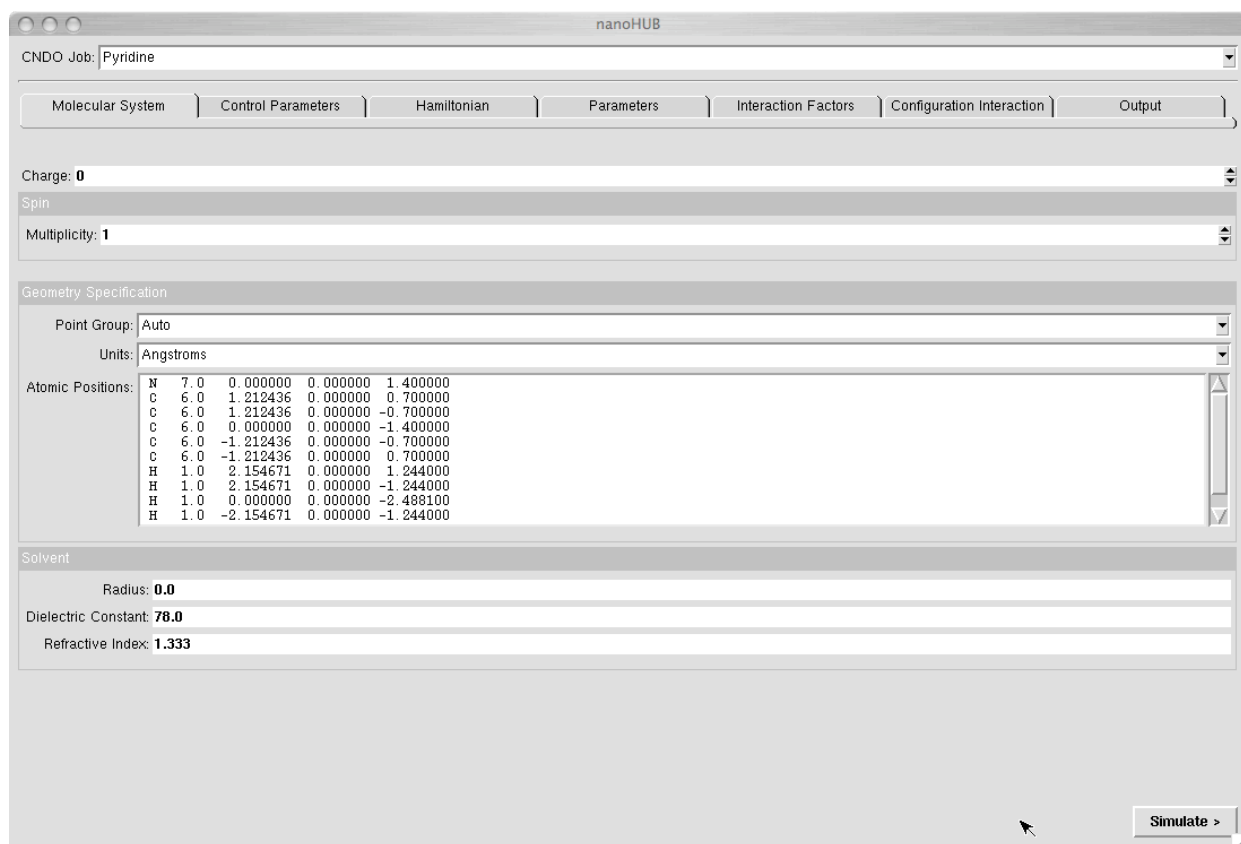

Figure 1: The tool CNDO/INDO showing the menu that controls the chemical model parameters for the molecule of pyridine: charge (0), spin multiplicity (1, singlet), geometry (Cartesian coordinates in Angstroms) and solvent specification parameters.

At this point we can continue the description of procedure with one of our target systems. The simplest model is the cluster $(CdSe)_6$ whose geometry is in the file Cd6Cd6.xyz (Make sure you have downloaded it already from the *Blackboard* and the file is located on an accessible folder on your computer). The next step will be to read (or upload) the information on that file (the geometry) 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. At this point 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 these two elements is crucial in the formulation of the theoretical model. An erroneous input on either one of them will bring about a system/computer error or even worse, meaningless results. By the *charge* parameter, we describe whether our system is an ion or a neutral species while the spin multiplicity indicates how the electrons configure the electronic structure of the system: As an electronic system, the particles must obey Pauli's exclusion principle so, depending on the parity of the number of electrons the system may be:

> *Closed shell*: The system contains an even number of electrons so that they are paired by different spins (–1/2 | +1/2). The total spin of the system S (the sum of the spins of all electrons in the system) is zero (S=0).

> *Open shell*: A system with an odd number of electrons implies that S will be a multiple of ½ depending on the number of unpaired electrons.

The overall spin state of the system is specified by the so-called spin multiplicity 2S+1, which may take the values 1, 2, 3, etc. We say then that the spin of the system is *singlet*, *doublet*, *triplet*, etc. respectively.

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

c) *Selection of the Hamiltonian*. Once the structure, charge and spin multiplicity have been defined, we should select the Hamiltonial operator that will be used to solve the Schroedinger equation. For this, select the tab "Hamiltonian" on the main window of the tool and select INDO. This option will automatically set up the equations and will 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 5).
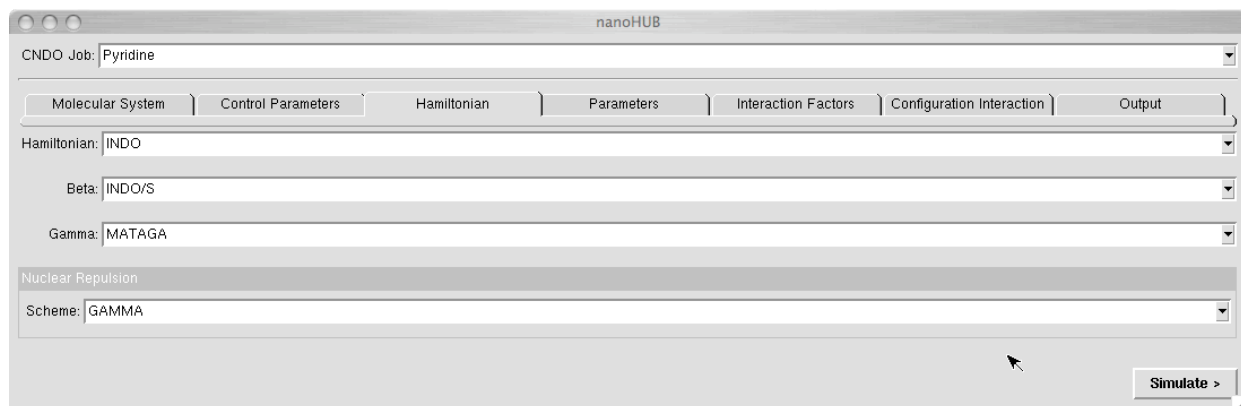
Figure 2: Selection of the Hamiltonian operator.

d) *Post-SCF calculation* (Configuration Interaction - CI). Once the HFRO equations ($\mathbf{F}\phi_i = e_i\phi_i$) have been solved, we need to determine the electronic states that the calculate structure may have access to. A way to accomplish this is by series expansion of the eigenvalues (E) and eigenvectors of the state function of the ($\mathbf{F}\phi_i = e_i\phi_i$) equations in a procedure called Configuration Interactions (CI). The elements of the expansion (Slater determinants) are constructed by taking the wavefunction as reference (calculated in the SCF procedure) and then exciting electrons from the occupied MOs to the virtual ones. Among all possible excitations, only those whose spin multiplicity complies with the total spin of the system imposed on section *b)*.
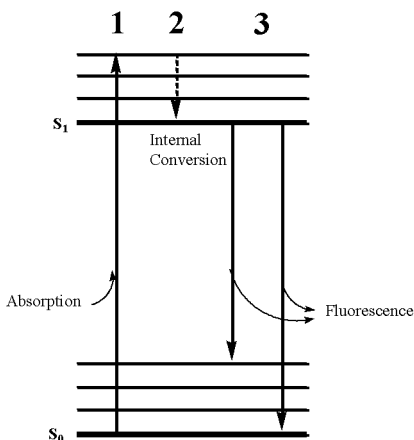

Figure 3: Jablonski Diagram

The program controls this option with the group under the tag "Configuration Interaction" on the GUI (see Figure 4). In general, we will be interested in obtaining the CI expansion of the same multiplicity of the ground state of the system; this is selected by the parameter "Mult_CI" (enter 1 for *singlet*, 2 for *doublet*, 3 for *triplet*, etc.). The menu option "Max_CI" determines the truncation of the CI expansion. The default 60 means that the wave function will be a linear combination of 60 Slater determinants. 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 virtual orbitals (empty) that may allocate the excited electron. Finally, specify that all excitation will be considered coming from the first state *i.e.*, the lowest in energy or ground state (set the Ex_From parameter to 1).

Figure 4: Configuration Interaction control panel.

The combination of these integer parameters is somewhat interdependent; in many cases the GUI, as well as the program operation, prevents from entering wrong or inconsistent values. In other cases, it is even able to detect them and automatically make the appropriate correction. However, after a job is submitted for run, it is a good practice to watch for messages on the GUI telling about the progress of the calculation. After the job has finished, there is a report and summary one can use for review it.

d) *Control Parameters:* These parameters are seldom changed. In special cases, when the default limit of SCF cycles (200) is reached the program stops but, it is possible however 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 circumstances 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 the geometry (coordinates, atomic numbers) and appropriateness of the spin multiplicity and/or charge of the system. These are common sources of problems.

Figure 5: Job control parameters. The default values are appropriate for most of the calculations so in general they do not need to be changed.

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.

III. Analysis of the output.

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

1.- *Molecular Structure and MO Energy diagram*. On Figure 6 are shown the 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 frontier orbitas 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.
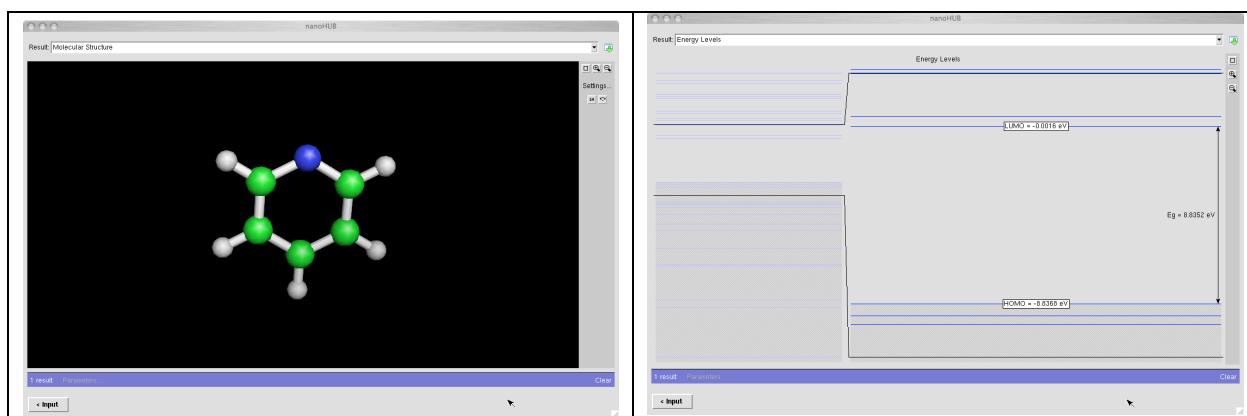

Figure 6: Representation of the molecular structure and the energy diagram of molecular orbitals.

2.- *Absorption Spectrum*. By selecting the appropriate option on the "Results" menu, you can visualize the theoretical UV/Vis absorption spectrum. The fFigure 7 shows the spectrum of the 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 permit to reset the view or select/unselect specific curves when multiple values are plotted on the same graph. It is possible to download the plot either as image or row 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 curve on

the desired point. Of special importance is the value of wavelength at which the substance shows a peak of absorption (λ_{max}).
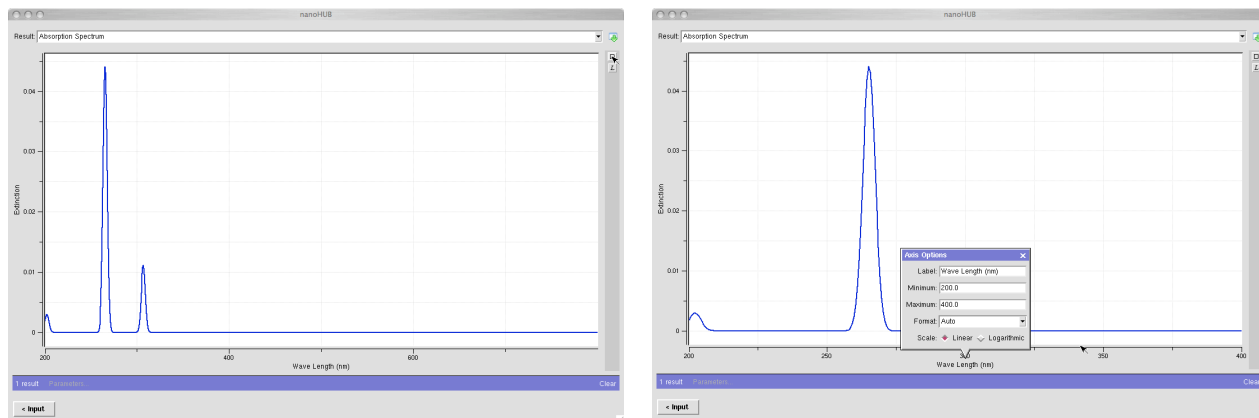

Figure 7: Calculated absorption spectrum of the molecule of pyridine. A section of the spectrum between 200 and 400nm is shown on the right.

4.- Log files. All the information that the program represents graphically is recorded in a log file and extracted from it. As such you may edited and search for specific numerical value (energies, dipole moments, basis functions coefficients, etc.). The report of the run is punched out on the section "Output log" of the "Results:" menu. To facilitate the search of data, you may find useful the *Find* text button at the bottom of window as illustrated in Figure 8. In this case, 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 iteration (SCF cycles) that the program needed to find HF solution. 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 ϕ_i solution of $\mathbf{F}\phi_i=e_i\phi_i$, preceded by their corresponding eigenvalues e_i, the orbital energies.

IMPORTANT: If the SCF did 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 our model make sense?) *ii)* review the charge and spin multiplicity. This is the first point one should look at before taking any further step.

If the SCF converged, the CI calculation follows. In the first step, the converged solution of the HF equations is taken as reference and from it the electron excitations are carried out to obtain the appropriate (Spin adapted) Salter determinants that compose the CI wave function. This step is shown on Figure 9; 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 a minimum on the energy, which will be taken as reference or ground energy by assigning it the zero value. The energy of the excited states will be obviously higher in energy. The Figure 10 shows the part of the log file in which you can read these parameters. The Jablonski diagram may be calculated from these energy values. We should note that from the conditions of the calculation, only information on the singlet states is reported.

Figure 8: Section of the *Output Log* file showing the total and electronic energies (in *eV*) after a successful, 26-iterarion SCF calculation.

Figure 9: Construction of the CI expansion.

```
            0.00  0.00  0.65  0.02  0.00  0.00  0.00  0.00
 52  B2107113.  2.00  2.00  2.00  2.00  2.00  2.00  2.00  1.05  1.99  1.97  1.99  2.00  2.00  0.00  0.01  0.00  0.01  0.95  0.00
            0.02  0.01  0.00  0.00  0.00  0.00  0.00  0.00
 53  A2108131.  2.00  2.00  2.00  2.00  2.00  1.39  1.68  1.99  2.00  1.94  2.00  2.00  2.00  0.01  0.62  0.37  0.00  0.00  0.00
            0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
 54  A2109549.  2.00  2.00  2.00  2.00  1.93  1.99  1.99  2.00  2.00  1.99  2.00  1.16  1.95  0.07  0.01  0.03  0.00  0.00  0.00
            0.00  0.00  0.00  0.05  0.83  0.00  0.00  0.00
 55  A2109741.  2.00  2.00  2.00  2.00  1.41  1.96  1.84  2.00  2.00  1.91  2.00  1.89  2.00  0.60  0.05  0.24  0.00  0.00  0.00
            0.00  0.00  0.00  0.00  0.11  0.00  0.00  0.00
 56  B2112168.  2.00  2.00  2.00  2.00  2.00  2.00  2.00  1.98  2.00  1.03  2.00  2.00  2.00  0.00  0.00  0.00  0.00  0.02  0.01
            0.96  0.00  0.00  0.00  0.00  0.00  0.00  0.00
 57  B1112593.  2.00  2.00  2.00  2.00  1.06  1.98  2.00  1.97  2.00  2.00  1.99  2.00  2.00  0.02  0.94  0.04  0.00  0.00  0.00
            0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
 58  A1112909.  2.00  2.00  2.00  2.00  2.00  2.00  2.00  1.05  1.97  2.00  1.98  2.00  2.00  0.00  0.00  0.03  0.02  0.00  0.93
            0.00  0.00  0.00  0.02  0.00  0.00  0.00  0.00
 59  B1115398.  2.00  2.00  2.00  2.00  2.00  2.00  2.00  2.00  1.09  2.00  2.00  1.94  1.97  0.00  0.00  0.00  0.00  0.00  0.00
            0.93  0.01  0.01  0.03  0.01  0.00  0.00  0.00
 60  A1116380.  2.00  2.00  2.00  2.00  2.00  2.00  2.00  1.99  1.98  1.99  1.04  2.00  2.00  0.01  0.00  0.01  0.00  0.01  0.02
            0.00  0.00  0.07  0.88  0.00  0.00  0.00  0.00

 Depression of ground-state after CI=       0. cm**   Energy= -1075.0334951 eV
 Dipole moment=  0.000000  0.000000 -2.918181 tot=  2.918181 Debyes


1After CI for multiplicity= 1 EXCITING FROM state  1 at Energy=       0. of symmetry  A1

 CI  trans.   energy frequency wavelength oscillator ---------polarization---------   dipole    ------components-----  solvent shift
 st.  symm.    eV      cm-1      nm      strength     x         y         z       moment     x       y       z    Abs    Emiss

   2   B1    4.0440   32617.    306.59  0.011133  1.000000  0.000000  0.000000  0.775098  0.000   0.000   0.775
   3   B2    4.6757   37712.    265.16  0.044089  0.000000  1.000000  0.000000  2.756856  0.000   0.000  -2.757
   4   A2    5.4293   43790.    228.36  0.000000                                2.736791  0.000   0.000   2.737
   5   A1    6.1334   49469.    202.15  0.002950  0.000000  0.000000 -1.000000  3.584501  0.000   0.000  -3.585
   6   A1    6.6510   53644.    186.41  0.777344  0.000000  0.000000  1.000000  2.612222  0.000   0.000  -2.612
   7   B2    6.8155   54970.    181.92  0.935161  0.000000  1.000000  0.000000  3.149902  0.000   0.000  -3.150
   8   A2    6.9803   56300.    177.62  0.000000                                0.866430  0.000   0.000  -0.866
   9   B1    7.4404   60011.    166.64  0.001402 -1.000000  0.000000  0.000000  1.780795  0.000   0.000  -1.781
  10   B1    7.5979   61281.    163.18  0.005481  1.000000  0.000000  0.000000  3.510012  0.000   0.000   3.510
  11   B1    7.6370   61597.    162.35  0.000529 -1.000000  0.000000  0.000000  1.589067  0.000   0.000  -1.589
  12   B2    7.7761   62719.    159.44  0.001824  0.000000  1.000000  0.000000  2.256659  0.000   0.000  -2.257
  13   A1    8.0365   64819.    154.28  0.126017  0.000000  0.000000  1.000000  0.587172  0.000   0.000   0.587
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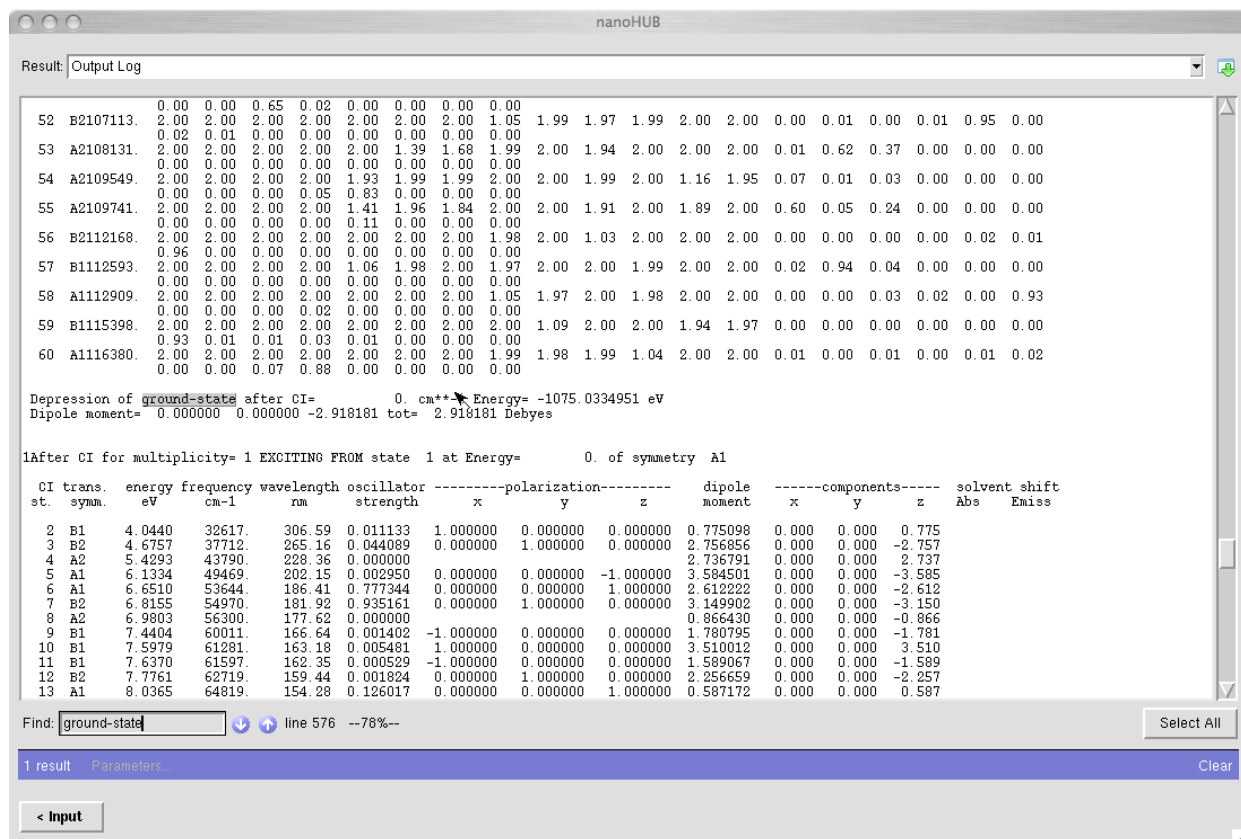
Figure 10: Location of the electronic states data. The strength of the oscillator (transition dipole moment) is related to the light absorbance of the material; these data is used to plot the UV/vis spectrum on Figure 7.

III.-Questions.
Assuming that the formation of CdSe particles is (thermodynamically) reversible process and that their crystalline structure is that of the crystal observed macroscopically (X-Ray diffraction)

1.- Write the chemical equations that express the formation of the particles and calculate the Energy of reaction. – relative stability.
2.- Electronic states: Is it possible that a system with an even number of electrons had an open shell electronic structure?
2b.- an hypothetical cluster Cd30Se31 has an even number of electrons. What would be its charge?
2.- Jablonsky diagram.
3.- Plot the absorption spectra and investigate the relationship between the size of the cluster and the calculated Lambda(max).

4.- Effect of the solvent.

x.- Extra bonus:
1.-Suggest a theoretical calculation that assess the observation of the elongated crystals.
2.- Effect of the nature of the solvent (donor).