Program for generating PDOS plots

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For an in-depth tutorial on how to run the program watch our YouTube tutorial on the PDOS program. Copy the following link in the browser:

https://youtu.be/mtJmazlh0c0

1. What does this program generate?

This program generates projected density of states (PDOS) plots which show the energy distribution of electrons in specific atom(s) in a material. It can also show the distribution of the empty density of states and can represent specific types of electrons such as: spin-up, spin-down, subshell populations (spdfg), bond order (BO) between a pair of atoms, and the sum of bond order (SBO) for an atom. The energy distribution of bond order is plotted as bond order components (BOCs) that are positive for bonding interactions and negative for anti-bonding interactions.

The program also generates a csv (PDOS_program_output.csv) file containing all the information required to plot the data manually without using the GUI program.

2. Required modules and programs

To run this program, you need Python 3.9 or above. You can install Python from python.org. Make sure it is added to the system path name (environmental variables). Make sure that pip is included in the installation.

The following libraries need to be installed through the command prompt:

- Numpy (pip install numpy)
- Matplotlib (pip install matplotlib)

3. Required input files

To run the program, place all the output files generated by the Chargemol program in a folder. Specifically, the files required by the program are:

DDEC_atom_volumes.xyz – This file contains the list of atoms in the system, their coordinates (in Å) and the volume of the atoms in $bohr^3$.

orbitals_info.txt – This file contains the total number of orbitals in the system, along with indicators for spin polarization and the availability of orbital energies. If energies are available, the file includes the orbitals, their occupancy, and corresponding energy values in hartrees. Please note that if no orbital energies are available the program will pop-up an error window saying there are no orbital energies available for the system.

BOCA.txt – This file contains the bond order component analysis (BOCA) for each of the atoms in the system. For each pair of atoms in the system, it includes the total bond order, spin-resolved bond orders (spin-up and spin-down), and BOCA parameters. Additionally, the file provides a

breakdown of the bond order by symmetry type (e.g., sigma, pi, delta) and lists individual orbital contributions, including their occupancy, bond order component (BOC), and energy values.

for a spin polarized system:

spin_up_orbital_spdfg_populations.txt and **spin_down_orbital_spdfg_populations.txt –** These files contain the spin-up and spin-down orbital populations, respectively, for each atom in the system, along with their corresponding energy values in hartrees.

spin_up_empty_DOS.txt and **spin_down_empty_DOS.txt –** These files contain the empty spin-up and spin-down density of states (DOS) of available orbitals, respectively, for each atom in the system, along with their corresponding energy values in hartrees.

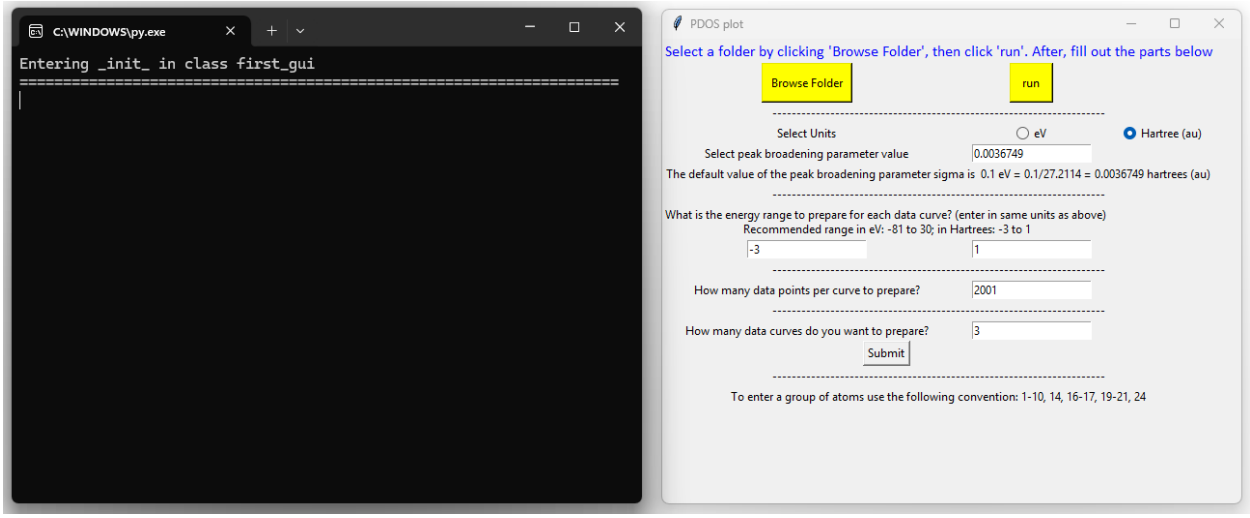
for a spin non-polarized system:

orbital_spdfg_populations.txt – This file contains the orbital spdfg populations for each atom in the material, along with their corresponding energy values in hartrees.

empty_DOS.txt – This file contains the empty DOS of available orbital spdfg populations for each atom in the material, along with their corresponding energy values in hartrees.

4. Running the PDOS program:

For both spin polarized and non-polarized systems you will need to run the PDOS python file PDOS_program.py. Upon launching the program, the following windows will appear:



The right panel is the GUI where you will perform all tasks while the left panel is the Python interpreter window. Click the **Browse Folder** button to open a file explorer window. Select the folder containing the input files. Note that while individual files may not be visibly listed in the directory, they are still present and accessible to the program.

Once a folder is selected click the **run** button. After, information about the system is going to be printed in the Python interpreter window.

Select Units is where you will have the option to select the units: eV or Hartree (au).

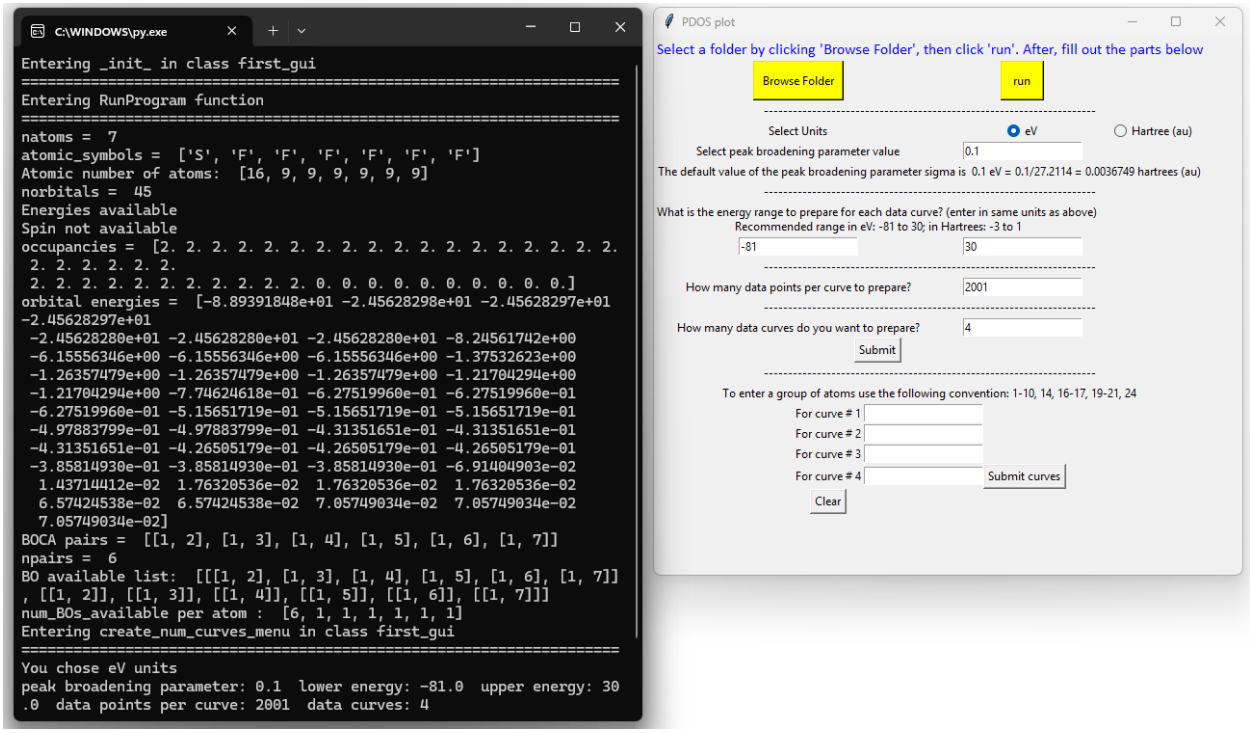
The **Select smearing parameter value** only affects the sharpness of the peaks and does not affect the total integral of any curve. For appearance purposes we recommend using 0.1 eV or its equivalent in hartrees.

What is the energy range to prepare for each data curve? This is going to be the x-axis of your plot. For a typical scenario, we recommend -81 to 30 eV or -3 to 1 hartrees. However, the specific range depends on what you are trying to show in your plot. If you want to show both core and valence electrons in your PDOS plot, then you need to select an appropriate energy range that depends on the chemical elements present in your system. The core electrons are located at deeply negative energies, while the valence electrons are located at shallower energies.

How many data points per curve to prepare? This is the number of data points you want to create between the limits set for your x-axis with a uniform increment among them.

How many data curves do you want to prepare? This is the number of total curves you want in your PDOS plot.

After clicking the **Submit** button, a new menu will appear prompting you to enter the atom number for which you want to generate curves. To identify the element's symbol, refer to the Python interpreter under the `atomic_symbols` tag. Alternatively, you can check the atom numbers in the DDEC_atom_volumes.xyz input file.

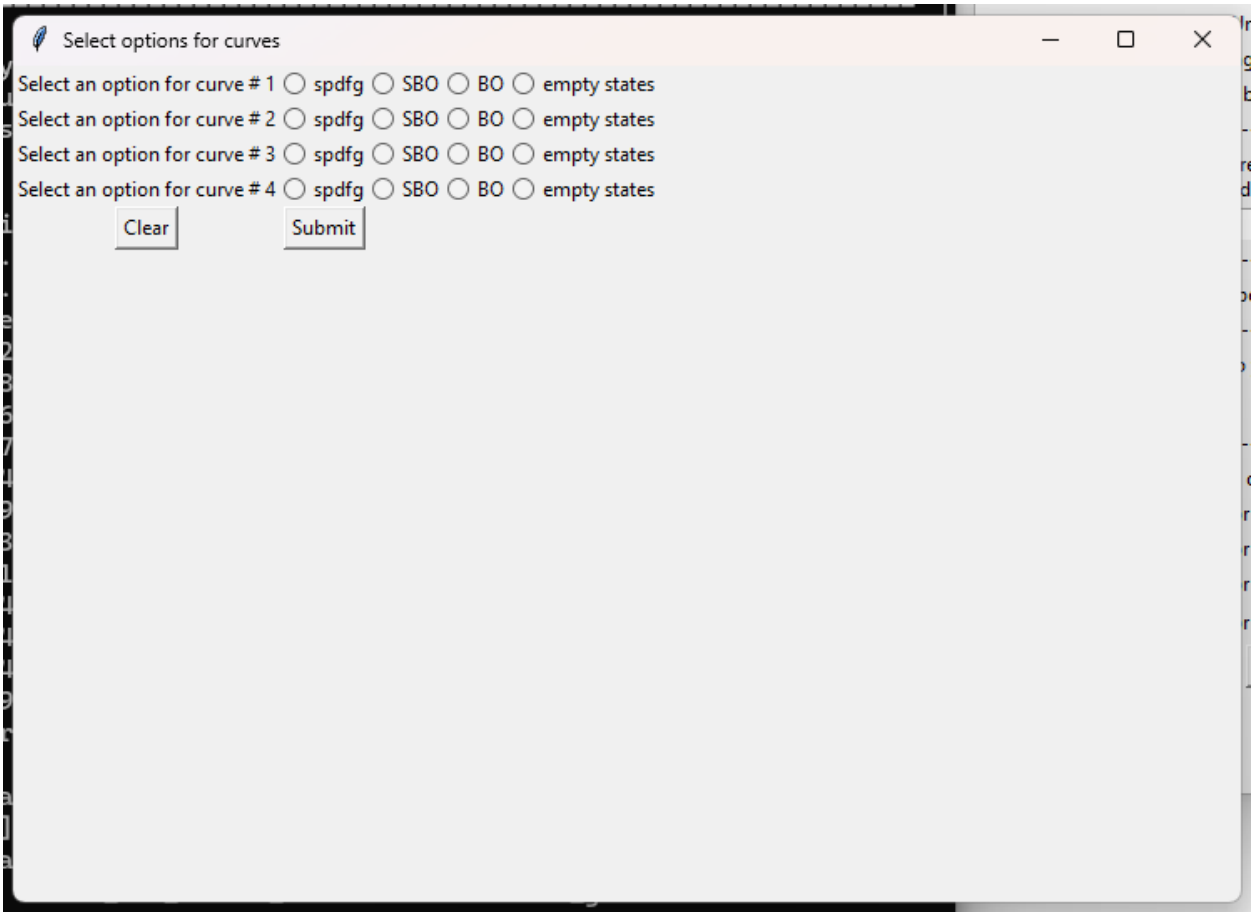


Enter a group of atoms for each curve: This selects which atoms will be included in the PDOS data used to generate each curve. If a range of atoms is specified, then PDOS for all of the atoms in that range are included. For example, if an organic molecule contains carbon atoms as atom #'s 1,2,3,4,10,20,21, you could specify th list '1-4, 10, 20-21' to generate the combined PDOS for all of the carbon atoms in the material plottes as curve #1. For curve #2, you can choose any range of atoms, which doesn't have to be the same atoms as used for curve #1. For example, you might choose to plot the PDOS for atom #13 in curve #2.

In the SF_6 molecule example illustrated below, to explore the sulfur atom in the system, enter number 1 in each of the blank lines that appear.

The **Clear** button resets your selection, allowing you to input a new number of data curves to generate.

Clicking the **Submit curves** button submits your selections and opens a new window with options based on the selected system.



Make your desired selections. If you change your mind, click the **Clear** button to close the current window and return to the previous menu where you selected the atom number to explore. For spin polarized systems the options will display separate selections spin-up and spin-down electrons for the spdfg electrons and the empty states.

After clicking **Submit**, a dropdown menu will appear next to each selection. Use these dropdowns to adjust your choices as needed. If you decide to change your selections, it is crucial to click the **Clear** button that appears in this step before submitting again. Failing to do so may result in incorrect outputs.

Dropdown menu selections for spin non-polarized calculations:

spdfg selection: Choose to display electrons from one of the s, p, d, f, g, or all orbitals. These curves will appear as solid lines.

SBO selection: the only selection you can choose is the SBO for the selected atom.

BO selection: Choose a BO corresponding to one of the atoms connected to the one you are analyzing.

empty states selection: Choose to display electrons from one of the s, p, d, f, g, or all virtual orbitals. These curves will show with dotted lines.

Dropdown menu selections for spin polarized calculations:

spdfg spin-up, spdfg spin-down, or spdfg selections: Choose to display electrons from spin-up, spin-down, or spin-up and spin-down for one of the s, p, d, f, g, or all orbitals. These curves will appear as solid lines.

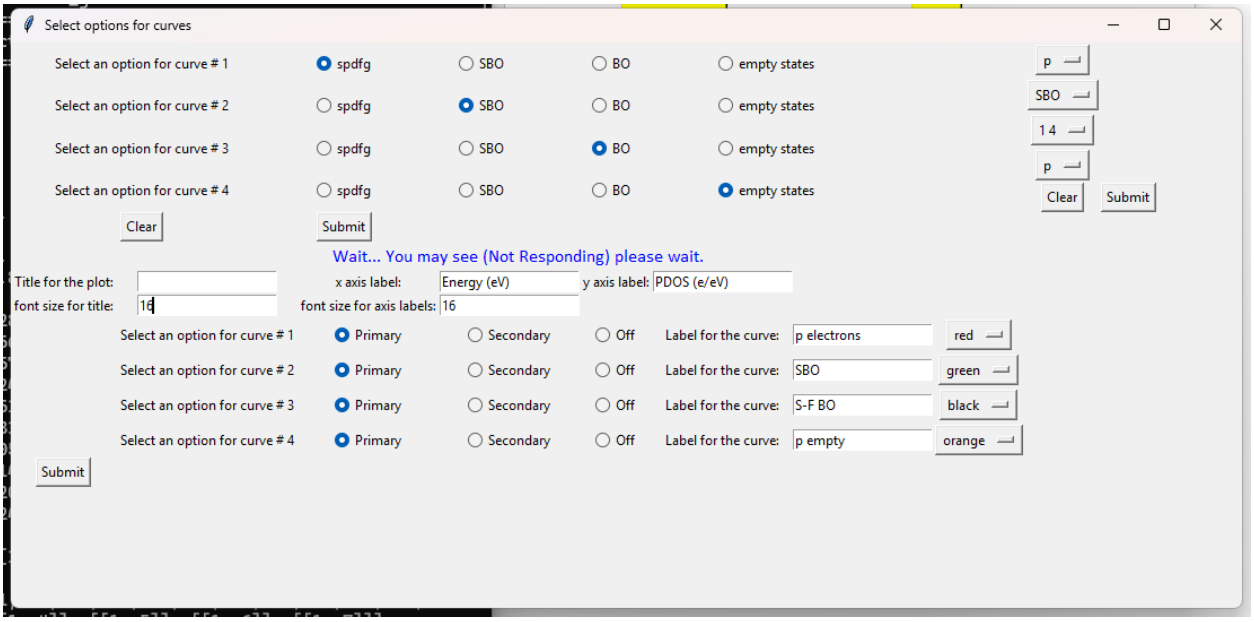
SBO selection: Choose between spin-up SBO, spin-down SBO or total SBO for the selected atom.

BO spin-up, BO spin-down, or BO selection: Choose from spin-up, down or total BO corresponding to one of the atoms connected to the one you are analyzing.

empty states spin-up, empty states spin-down, or empty states selection: Choose to display electrons from spin-up, spin-down, or both spin-up and spin-down for one of the s, p, d, f, g, or all virtual orbitals. These curves will appear as dotted lines.

After making your selections, click the **Submit** button. Additional plot options will then appear.

During this step, the program will generate the PDOS_program_output.csv file. Such file will be added to the directory you selected at the beginning. Please note that the program may briefly display a ‘Not Responding’ message, this is normal. Simply wait until the next set of options appears.



You will have the option to input a title for the plot, as well as labels for the x-axis and y-axis, including their respective font sizes.

For each curve you can choose to:

Primary selection to plot it on the primary axis.

Secondary selection to move it to a secondary axis.

Off selection to make the curve invisible.

You will also have the option to assign a label to each curve and select its color using a dropdown menu.

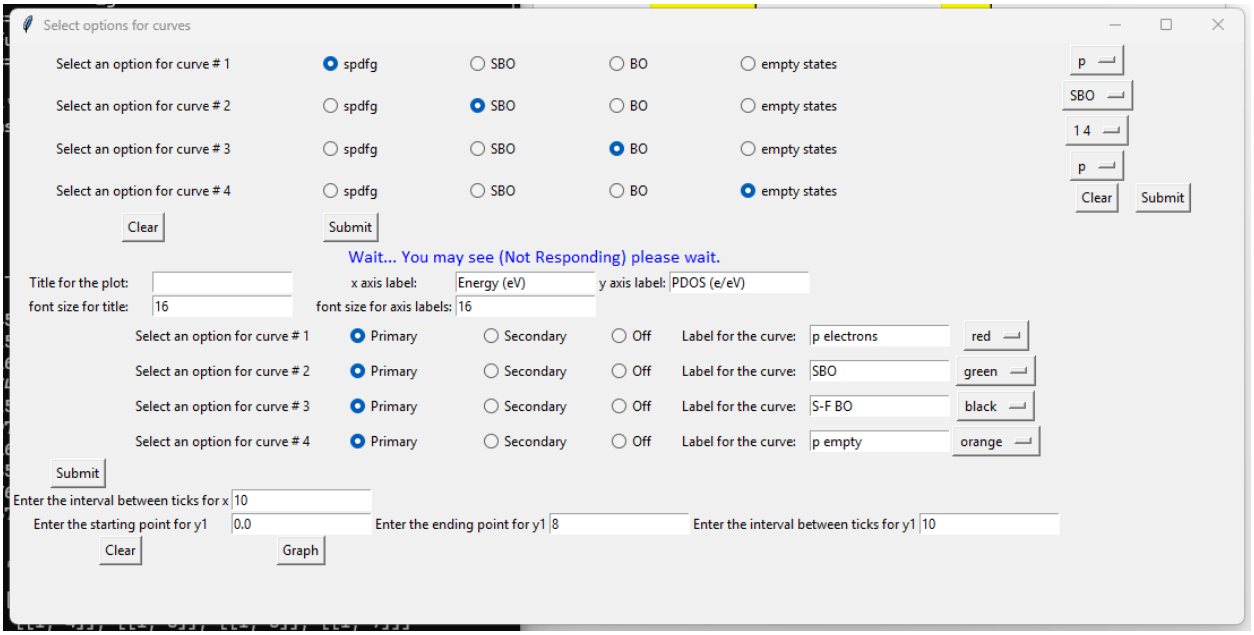
After clicking the **Submit** button, you will be prompted to provide:

The interval between ticks for the x-axis,

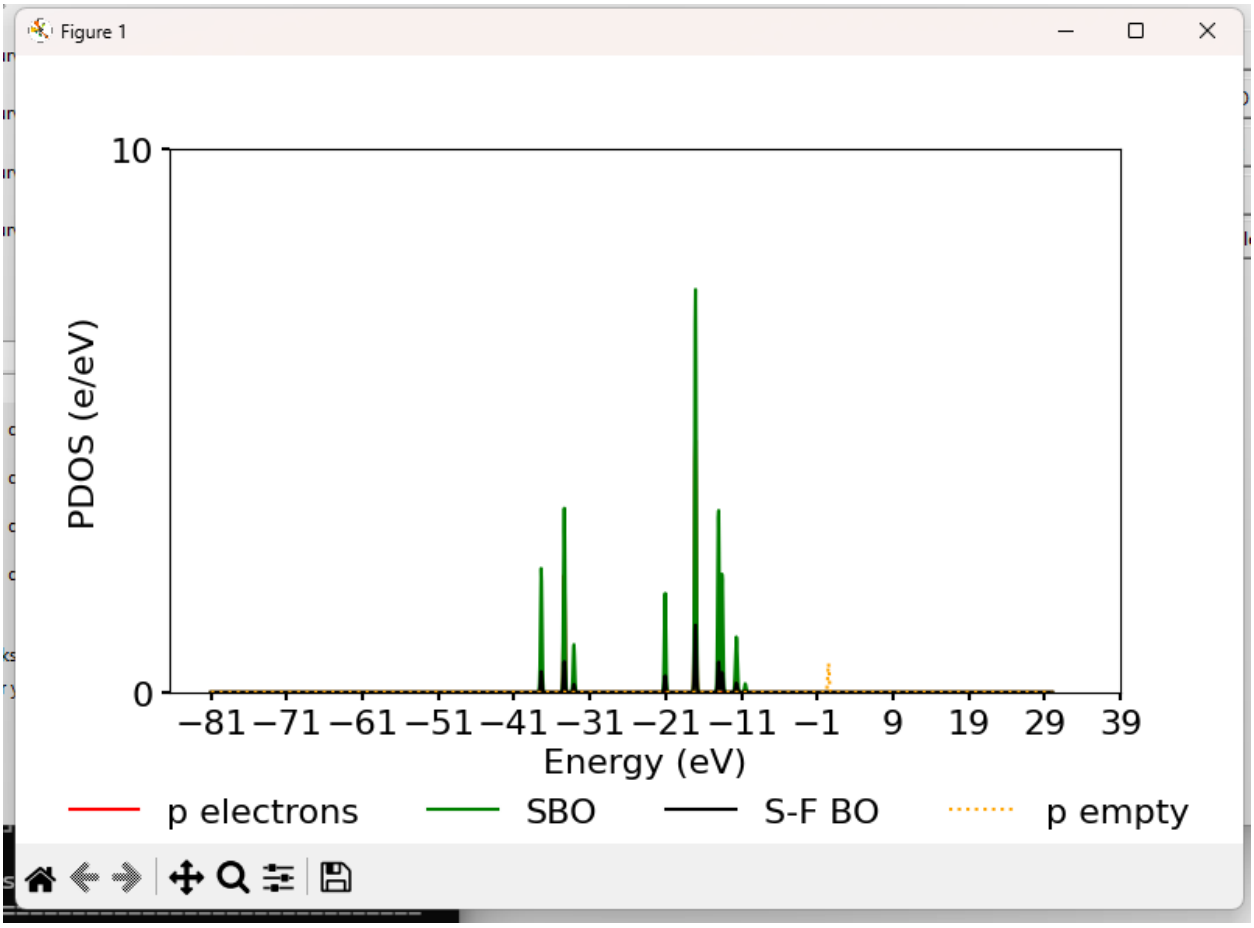
The starting point for the y-axis,

The ending point for the y-axis (the program will automatically determine the maximum y-axis value for all curves), and

The interval between ticks for the y-axis.



The **Graph** button will display a new window with the plot. This window can be resized.



The selections for the plot are as follows:

Pan tool: Allows you to move the plot area around.

Zoom tool: Enables zooming into a specific area of the plot.

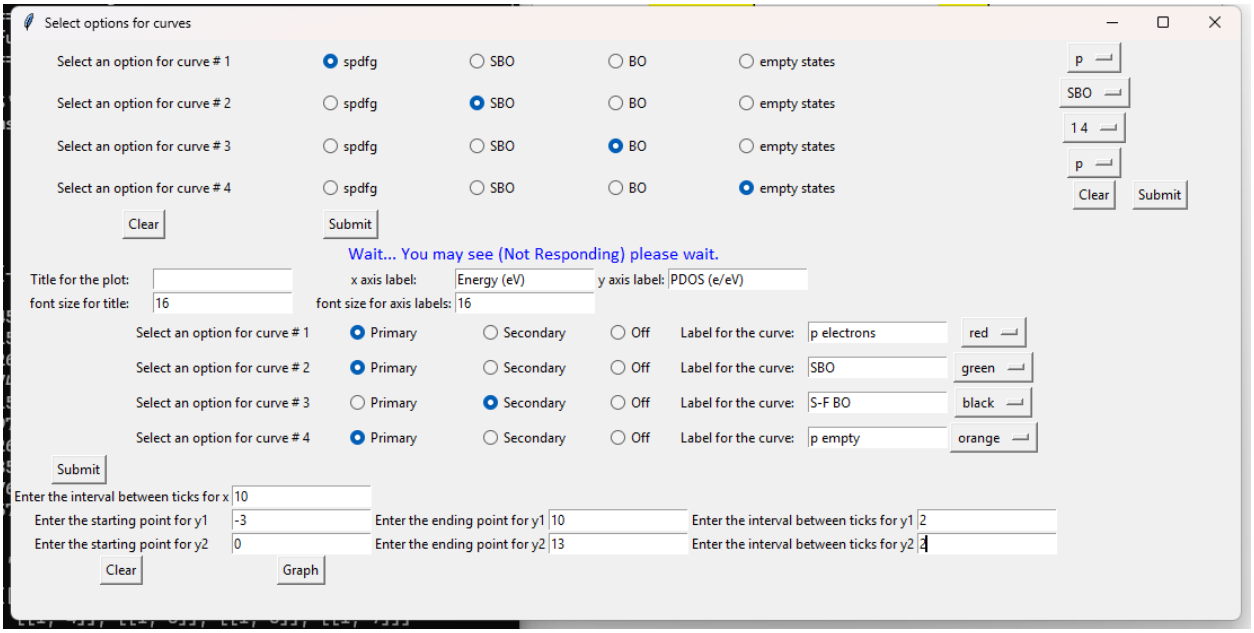
Undo/Redo: Lets you undo, or redo changes made to the plot view.

Reset view: Restores the plot to its original view from when the window was first opened.

Subplot configuration tool: Opens a menu with sliders that allow you to adjust the whitespace in the plot.

Save the figure: This option allows you to choose where to save the plot as it appears in the window. By default, the plot is saved in .png format, but you can select other formats such as .jpeg, .jpg, .pdf, .tiff, and more, depending on your preference.

After the initial viewing of the plot, it may be helpful to move some curves to a secondary axis. For example, if the highest point of the curve you want to move to a secondary axis is around 3 eV in the y-axis, you can adjust the selections. First, press the **Clear** button in the last menu selection. Once the menu disappears, select Secondary for the curve you wish to move. To position the secondary axis below the primary axis, shift the primary axis starting point by -3 and extend the secondary axis endpoint by adding 3 to the primary axis maximum. After setting appropriate tick intervals, click **Graph** to update the plot. This adjustment can improve clarity and ensure all curves are easily distinguishable.



The following plot shows the results:

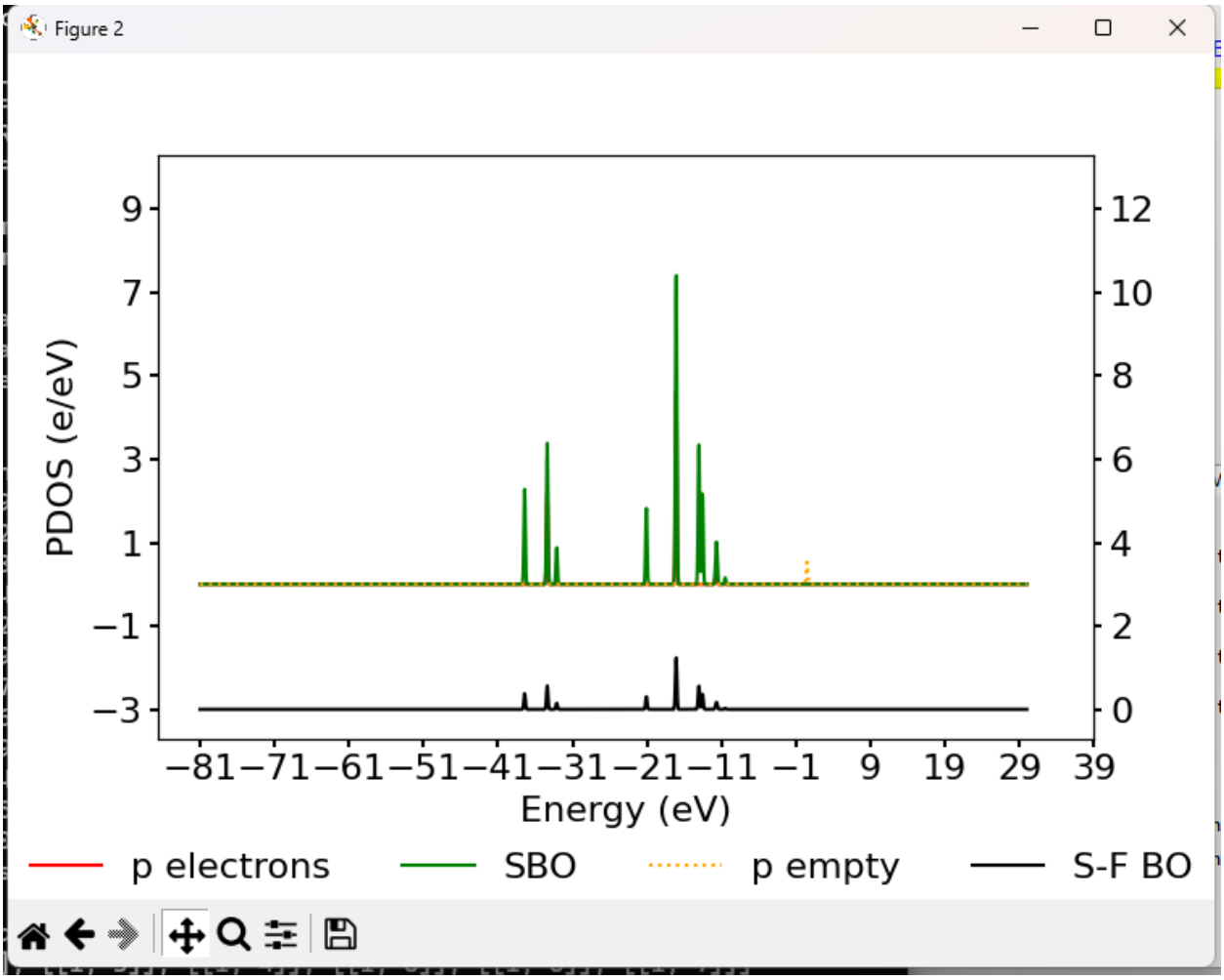


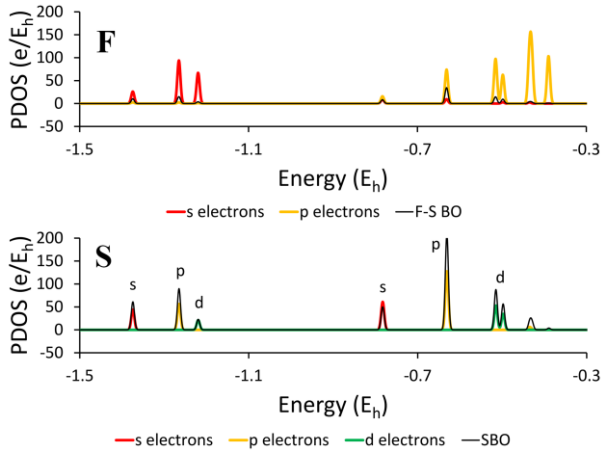
Figure 2
PDOS (e/eV)
9
7
5
3
1
−1
−3
12
10
8
6
4
2
0
−81 −71 −61 −51 −41 −31 −21 −11 −1 9 19 29 39
Energy (eV)
p electrons
SBO
p empty
S-F BO

5. Explaining PDOS plots:

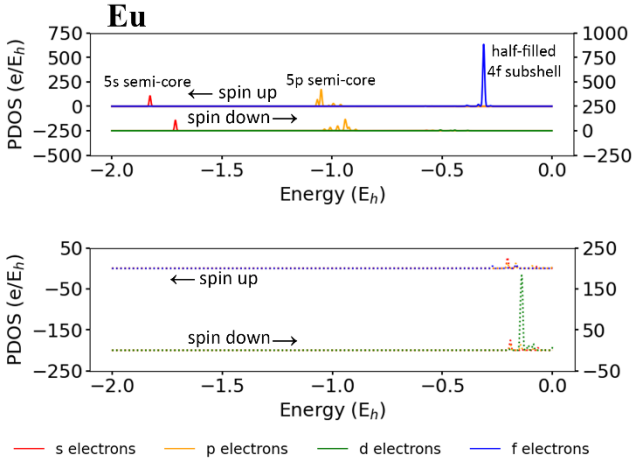
The following PDOS plot represents the spin non-polarized SF_6 system, showing the PDOS for a single fluorine atom. The fluorine valence 2s electrons are observed in three peaks between -1.35 and -1.15 E_h, while the 2p electrons appear between -0.7 and -0.3 E_h.

For the sulfur atom, the 2s electrons are located around -1.4 E_h, the 3s electrons at -0.77 E_h, the 2p electrons at -1.26 E_h, and the 3p electrons at -0.6 E_h. Most of the sulfur 3d electrons are observed around -0.5 E_h, with a small number located around -1.2 eV.

All sulfur valence orbitals correspond to bonding interactions (i.e., positive BOCs). In contrast, the fluorine PDOS shows non-bonding contributions (i.e., negligible SBO or BO) near -0.38 E_h, attributed to its lone pair electrons. No anti-bonding interactions (i.e., negative BOCs) are present in this system.



The following PDOS plot represents the spin polarized $[Eu@C_{60}]^+$ system. It shows the PDOS distributions for the europium atom in the system. The Eu atom in this molecule has a half-filled 4f subshell at -0.3 E_h, along with partially hybridized 5p semi-core electrons around -1.0 E_h and 5s semi-core electrons around -1.5 to -1.8 E_h. As shown, all the electrons in the 4f subshell are spin-up. In the lower panel, the spin-down virtual orbitals appear at higher energies than all occupied orbitals, as expected.



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Manz, T. A., Chen, T., Escobosa, A. C. "Bonding subshell analysis: part 3. Electron categorization via bond order components and projected density of states plots" *RSC Advances* (In preparation)