AVOGADRO with YAEHMOP Manual

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1 Installation

1.1 Windows

The Windows binary may be downloaded from the following location:

`https://avogadro-yaehmop.github.io/`

The file may be unzipped using any unzipping software. 7-Zip [1] is a good option if unzipping software is not installed. After the file has been unzipped, double click on the executable that is inside, and proceed through the security warning. Go through the install process using all of the default options (you may want check the box to "Create Avogadro Desktop Item"). Note that if AVOGADRO is already installed, this installation will replace it. This installation may be installed in a different location if replacing the current AVOGADRO is not desired. Once the installation finishes, it can be opened with the desktop icon or through the start menu. It may be uninstalled either through "Add or remove programs" or through the uninstaller that is located in the install location (most likely "C:\Program Files (x86)\Avogadro").

1.2 Mac

The Mac binary may be downloaded from the following location:

`https://avogadro-yaehmop.github.io/`

If the file does not unzip automatically, it must be unzipped manually. Once this is done, the AVOGADRO application can be found inside. Double clicking may not open the file for security reasons. It may be necessary to right click the application, click "Open", and then accept it despite the warning. It may also be added to the applications by copying and pasting it into the /Applications directory. To uninstall it simply delete the application file.

1.3 Linux

The Linux binary may be downloaded from the following location:

`https://avogadro-yaehmop.github.io/`

This file may be unzipped through the GUI or the terminal (using the "tar -xzvf linux-avogadro-yaehmop.tgz" command). In the unzipped and untarred directory, the Avogadro executable is "avogadro-yaehmop/bin/avogadro". The whole "avogadro-yaehmop" directory may be moved, but the files that are inside it cannot be moved or changed. The program may be uninstalled by simply deleting the directory.

2 Tuning the extended Hückel parameters

The accuracy of the extended Hückel calculations can be improved by fitting the EHT parameters to *ab initio* data. Herein, the Fredrickson group's extended Hückel tuner [2, 3] that is designed specifically to fit parameters in YAeHMOP to VASP [4] data was employed.

In the fitting procedure, the ionization potentials were kept constant, and all other parameters were optimized. The fits were performed for graphite (to VASP-PBE calculations), silicon (to VASP-HSE06 calculations), and sodium (to VASP-PBE data). HSE06 was used for the semiconductor, silicon, because this screened hybrid functional is known to predict band gaps that agree more closely with experiment than PBE, which typically underestimates band gaps.

The following are the fit parameters that were employed (in the same format that YAeHMOP expects them):

Graphite:

C 6 4 1 2 s −21.400 1.9033 0.0000 1.0000 0.0000
C 6 4 1 2 p −11.400 1.7622 0.0000 1.0000 0.0000

Silicon:

SI 14 4 1 3 s −17.300 1.7131 0.0000 1.0000 0.0000
SI 14 4 1 3 p −9.200 1.4145 0.0000 1.0000 0.0000
SI 14 4 2 3 d −2.333 5.3866 1.0054 1.0560 1.6018

Sodium:

```
NA 11 1 1 3 s −5.100 1.0416 0.0000 1.0000 0.0000
NA 11 1 1 3 p −3.000 1.3324 0.0000 1.0000 0.0000
```

The default parameters were used for diamond.

To use one of these sets of parameters, copy and paste these lines to a blank file, choose "Extensions"→"Yaehmop"→"Set Parameters File..." from the Avogadro interface, and then select the file containing the parameters. While Avogadro is still open, the rest of the YAeHMOP calculations will use these parameters (note that if the parameters file only contains one type of element, calculations cannot be performed involving any other type of element while the file is open, and YAeHMOP will fail to run).

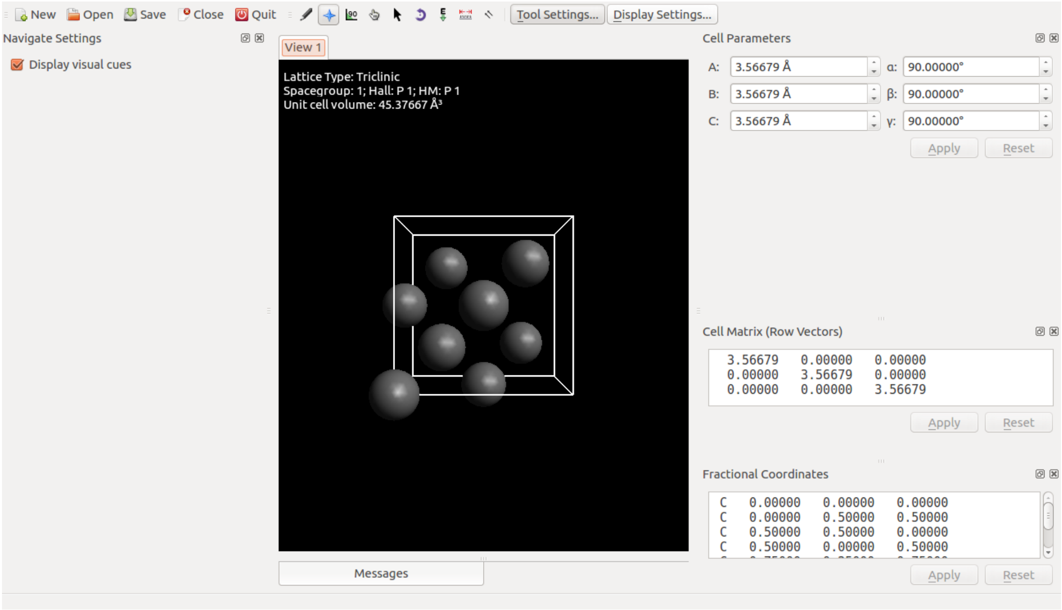
3 Notes on Options

Before we begin, it should be noted that the original YAeHMOP manual can be found at https://github.com/greglandrum/yaehmop/blob/master/docs/bind_manual.pdf. Many of the options described in the original manual, however, are not customizable in our implementation. This is because we wanted to automate the most frequently used options for ease of use. It is, however, possible to input custom options via the "Execute Custom Input..." option; however, if this is done, the YAeHMOP output is simply shown, but the results will not be plotted via the graphical user interface (GUI).

4 Preparation for Densities of States (DOS) or Band Structure

This section includes the general setup that is needed for a DOS or band structure calculation. Diamond, a known insulator, will be used as an example.

After Avogadro has been opened, click "Open" in the top left corner, and navigate through the file dialog to the "crystals" directory. Diamond is located in "elements" and it is named "C-Diamond.cif". Open this file. Note that if the file is grayed out and cannot be opened, it may be necessary to change the file types at the bottom of the file dialog to "All files" (on Mac, the "Options" button must be clicked first). Once the file has been opened, diamond should appear on the screen as it does in Fig. 1. Note that this is a conventional cell, not a primitive cell.



☑ Display visual cues

```
Lattice Type: Triclinic
Spacegroup: 1; Hall: P 1; HM: P 1
Unit cell volume: 45.37667 Å³
```

Cell Parameters

A: 3.56679 Å α: 90.00000°

B: 3.56679 Å β: 90.00000°

C: 3.56679 Å γ: 90.00000°

Cell Matrix (Row Vectors)

```
3.56679   0.00000   0.00000
0.00000   3.56679   0.00000
0.00000   0.00000   3.56679
```

Fractional Coordinates

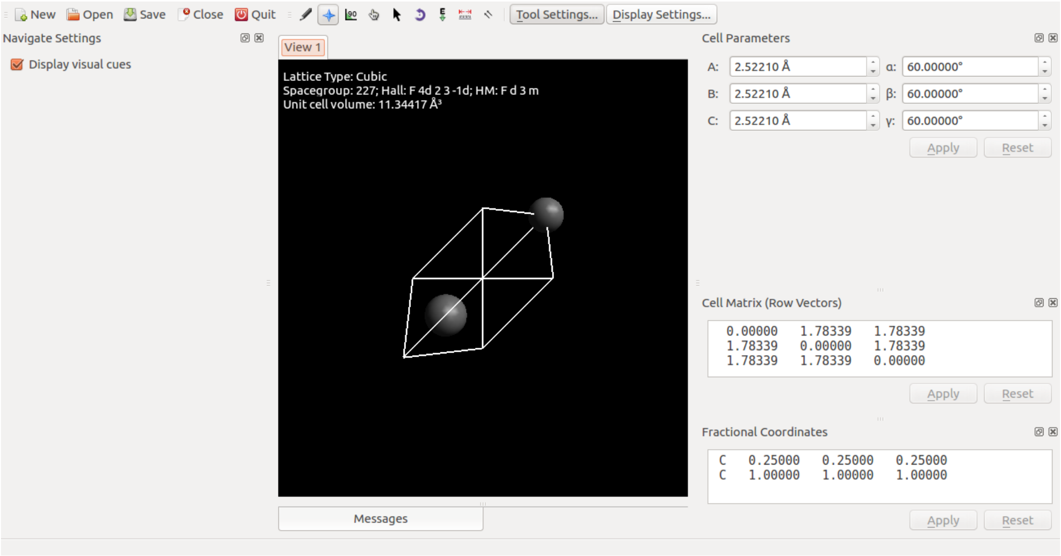
```
C   0.00000   0.00000   0.00000
C   0.00000   0.50000   0.50000
C   0.50000   0.50000   0.00000
C   0.50000   0.00000   0.50000
```

Figure 1: Diamond in its conventional cell

Although band structures can be calculated with non-primitive cells, they will give "back-folded" band structures. Thus, it is common practice to reduce a cell to its primitive form before performing the calculations. As for the orientation, it is important to note that the three-dimensional points in reciprocal space depend upon the orientation of the cell in real space. It is necessary to make sure, then, that the orientation is standardized. The proper orientation depends on the Bravais lattice of the cell.

Both of these operations (primitive reductions and cell standardization) can be done in one operation in Avogadro. First, the space group tolerance needs to be set to a reasonable value. Click "Crystallography"→"Settings"→"Tolerance for symmetry operations...". Change the tolerance to be 0.0001 and press "OK". Next, click "Crystallography"→"Reduce"→"Reduce

Cell (Primitive and Standardize)".



Lattice Type: Cubic
Spacegroup: 227; Hall: F 4d 2 3 -1d; HM: F d 3 m
Unit cell volume: 11.34417 Å³

Cell Parameters

A: 2.52210 Å
B: 2.52210 Å
C: 2.52210 Å
α: 60.00000°
β: 60.00000°
γ: 60.00000°

Cell Matrix (Row Vectors)

```
0.00000   1.78339   1.78339
1.78339   0.00000   1.78339
1.78339   1.78339   0.00000
```

Fractional Coordinates

```
C   0.25000   0.25000   0.25000
C   1.00000   1.00000   1.00000
```

Figure 2: Diamond in its primitive cell

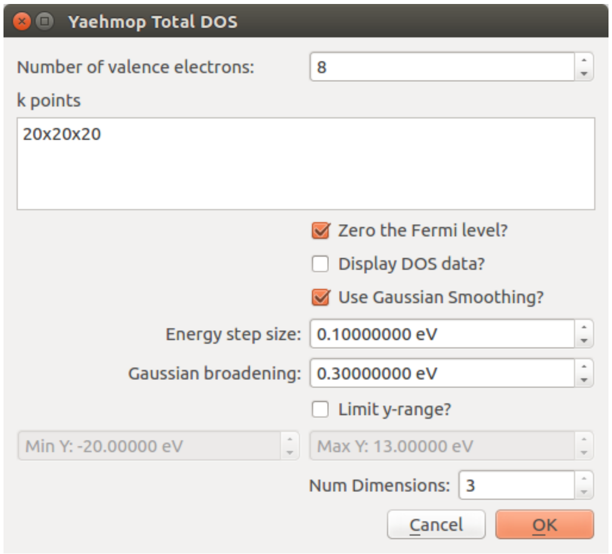
When these steps are completed, diamond should look as shown in Fig. 2. In addition to there only being two atoms in the unit cell now, the actual shape of the cell will have changed. The top left corner should now display the lattice type and space group (*Fd-3m*) correctly.

5 DOS Calculations

DOS calculations can be used to determine the number of states within a particular energy window. Because they are also the most accurate method of determining the Fermi energy, they should be performed before a band structure calculation.

Within AVOGADRO click "Extensions"→"Yaehmop"→"Calculate Density of States". A dialog box similar to the one shown in Fig. 3 should appear. The options for this calculation should be set to match that of Fig. 3.

The "Number of valence electrons" will automatically be generated using the atoms in the unit cell. This number may be adjusted (one reason for changing it would be if an atom were charged, for example). Because herein the calculations are carried out on a neutral cell



Number of valence electrons: 8

k points
20x20x20

☑ Zero the Fermi level?
☐ Display DOS data?
☑ Use Gaussian Smoothing?

Energy step size: 0.10000000 eV
Gaussian broadening: 0.30000000 eV

☐ Limit y-range?

Min Y: -20.00000 eV
Max Y: 13.00000 eV

Num Dimensions: 3

Figure 3: Density of states dialog box

containing two carbon atoms, the guess of "8" electrons is correct. The k-point mesh may be specified in the "k-points" box. The user can employ a regular mesh wherein the number of points along a reciprocal lattice vector should ideally be inversely proportional to the real space vector (such as 20 × 20 × 20 for a cubic cell). Sampling a larger number of points will yield more accurate results. However, be aware that if too many points for a system with too many atoms are employed, the operating system may shut down YAeHMOP while it is running (and Avogadro may continue as if it were not asked to calculate anything). Alternatively, k-points may be added using the format <x> <y> <z> <weight> where the weight is how many times the point is counted. For example, one can use the Monkhorst-Pack method within VASP to generate a list of k-points based on the symmetry of the lattice and copy and paste them into this dialogue box. Herein, a 20 × 20 × 20 mesh was employed. If YAeHMOP fails, a smaller mesh can be used.

The Fermi level is always calculated when doing a DOS calculation. Thus, checking the box "Zero the Fermi level?" automatically adjusts the data based upon the Fermi level. Please check this box.

"Display DOS data?" will display the data so that it may be copied and pasted into a file for replotting and analysis using external software. The unadjusted Fermi level is printed first in the displayed data, followed by the DOS values. Finally, if Gaussian smoothing was used, integration data is printed as well. Within this example, the DOS data does not need to be exported to another program, so leave the box unchecked.

"Use Gaussian Smoothing?" fits the data to Gaussian functions to make it look significantly smoother. It also enables the integration of the DOS. It is recommended to use Gaussian smoothing most of the time. Please be sure that "Use Gaussian Smoothing?" is checked.

"Energy step size" may only be used if "Use Gaussian Smoothing?" is checked. The smaller this number is, the larger the number of points that will be created during the smoothing procedure. Thus, a smaller energy step size results in a more resolved graph. Herein, a size of 0.1 eV is employed.

"Gaussian broadening" may also only be used if "Use Gaussian Smoothing?" is checked. This number represents σ in the Gaussian distribution. Larger σ values yield a smoother graph. Note, however, that larger Gaussian smoothing values may also lead to artifacts, for example a finite DOS at the Fermi level for a system that is a semimetal, semiconductor or insulator. For this reason, it may be prudent to experiment with different smoothing values, in particular smaller ones, and also to examine the band structure plots. For diamond and the graphite example used herein, a value of 0.3 eV was used.

If the "Limit y-range?" box is checked, the y-range of the displayed graph will be limited to be between "Min y" and "Max y". "Limit y-range?" can be unchecked for the purpose of this exercise. Note that if these values are set in the DOS dialog box, they will be changed in the band structure dialog to match.

Since diamond is a 3-dimensional system, the number of dimensions should be set to "3". Note that a 1-dimensional system has periodicity along the A lattice vector, and a 2-dimensional system has periodicity along the A and B lattice vectors.

When the selected options match those shown in Fig. 3, the DOS calculation can be started by pressing the "OK" button. After a few seconds of calculating (Avogadro will gray out while YAeHMOP is running... if it does not, then something is wrong with the calculation or installation), Fig. 4 should appear. The Fermi level is plotted as a dashed line. Note that these settings yield a band gap of 5 eV for diamond, accurately indicating that diamond is an insulator. If smoothing is used, the integration will be plotted as a blue line (and the axis for the blue line is at the top of the graph). Note that the seemingly periodic oscillations in the DOS that are evident in particular at energies 20 eV or higher are a result of the size of the k-mesh coupled with the smoothing and the choice in the Gaussian broadening. Larger k-meshes may be necessary to decrease the number of oscillations, but such meshes may be too large for desktop computers. The blue line crosses the Fermi level at the number of valence electrons, and it reaches double the number of valence electrons at the top of the graph.

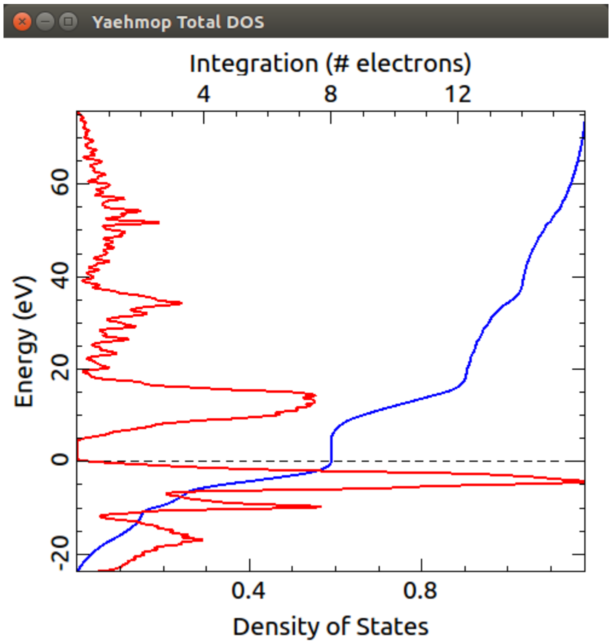


Figure 4: Density of states for diamond. The dashed line is the Fermi level.

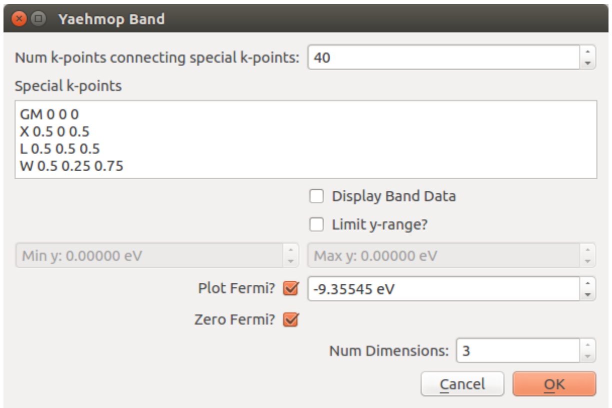
The user may zoom in on the graph, or they may translate the graph by holding right-click and dragging. If the user double-clicks the graph, it will return to its default axes.

That concludes the DOS exercise. Calculating the DOS of other materials, including those described in the manuscript, can be done in the same way. It is preferable to calculate the DOS before the band structure in order to obtain an accurate Fermi level for the band structure calculation (in fact, the Fermi level will be set automatically in the band structure dialog upon performing a DOS calculation).

6 Band Structure Calculations

Band structure calculations can also be very useful for obtaining information about the electronic structure of a solid, for example if it is metallic, semiconducting, or insulating. Note that the user may want to perform a DOS calculation first in order to obtain the correct Fermi level (as described in Section 5) if they have not done so. The unit cell should also be reduced to its primitive form and be given in its proper orientation (see Section 4) before performing the band structure calculation.

Within Avogadro click “Extensions”→“Yaehmop”→“Calculate Band Structure”. The dialog box in Fig. 5 should appear.



Num k-points connecting special k-points: 40

Special k-points

```
GM 0 0 0
X 0.5 0 0.5
L 0.5 0.5 0.5
W 0.5 0.25 0.75
```

☐ Display Band Data

☐ Limit y-range?

Min y: 0.00000 eV

Max y: 0.00000 eV

Plot Fermi? ☑ -9.35545 eV

Zero Fermi? ☑

Num Dimensions: 3

Figure 5: Band structure dialog box

The “Num of *k*-points connecting special *k*-points” is the number of points at which the energy will be calculated between each special *k*-point. Increasing this number increases the resolution of the plot, but decreases the speed of the calculation. Herein, 40 points are employed.

In the “Special *k*-points” section, special *k*-points will automatically be generated if the space group was correctly detected. The space group of the crystal is shown in the top left corner of the view (see Fig. 2). The user may detect the symmetry by reducing the cell to its primitive form or using the "Perceive Spacegroup" feature under "Crystallography"→"Spacegroup". If the space group is *P1* or undetected, only the Γ point will be present. The special k-points that are automatically generated are those that contain no variables. The list of these special k-points can be found for each space group on the Bilbao website [5]. Special k-points may be added, removed, or their order may be changed to vary the points and pathways that are explored in reciprocal space. For this example, the default special k-points will be used.

If the "Display Band Data" box is checked, the data will be printed to a dialog box that will be displayed after the calculation is complete. This data may be copied and pasted to plot with other software. Herein, the box can be left unchecked.

If the "Limit y-range?" box is checked, the y-range of the displayed graph will be limited to be between "Min y" and "Max y". Herein, this box can be left unchecked. Note that if these values are changed in the band structure dialog, the DOS dialog values will be adjusted to match.

If the "Plot Fermi?" box is checked, the Fermi level will be plotted as a dashed line, but the correct Fermi level needs to be given in the spinbox on the right. Because Fermi levels are obtained in a DOS calculation, the Fermi level spinbox will automatically be set to the value of the most recent DOS calculation. If a DOS calculation using the options above was just performed, this value will be set to -9.35545 eV. Fill in the box with the correct Fermi level (-9.35545 eV) if it is not set. For this exercise, "Plot Fermi?" should be checked and the correct Fermi level should be provided.

If the "Zero Fermi?" box is checked, all of the data will be adjusted so that the Fermi level is at zero. This cannot be set if "Plot Fermi?" is not checked because the Fermi level cannot be zeroed without knowing what it is. For this exercise, please check "Zero Fermi?"

Since diamond is a 3-dimensional system, the number of dimensions should be set to "3". Note that a 1-dimensional system has periodicity along the A lattice vector, and a

2-dimensional system has periodicity along the A and B lattice vectors.

Once all of the options given in Fig. 5 are set pressing the “OK button will yield a band structure plot that looks like Fig. 6. The Fermi level is plotted as a dashed line. Note that these settings yield a band gap of 5 eV that occurs at the Γ point for diamond, accurately indicating that it is an insulator.

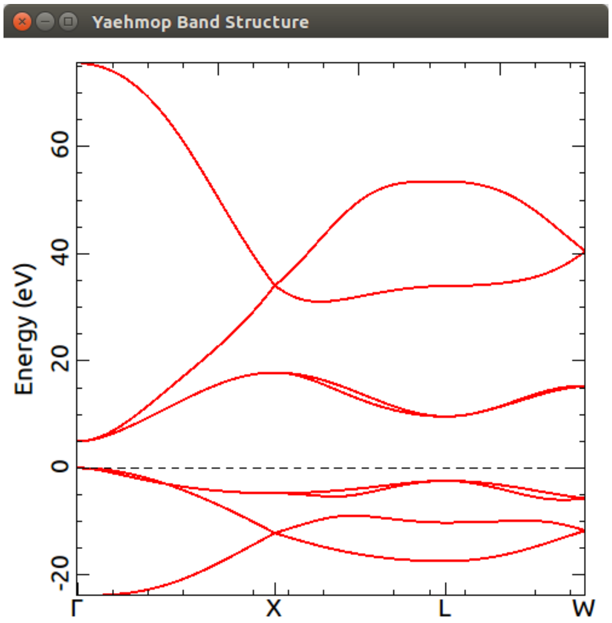


Figure 6: Band structure for diamond. The dashed line is the Fermi level.

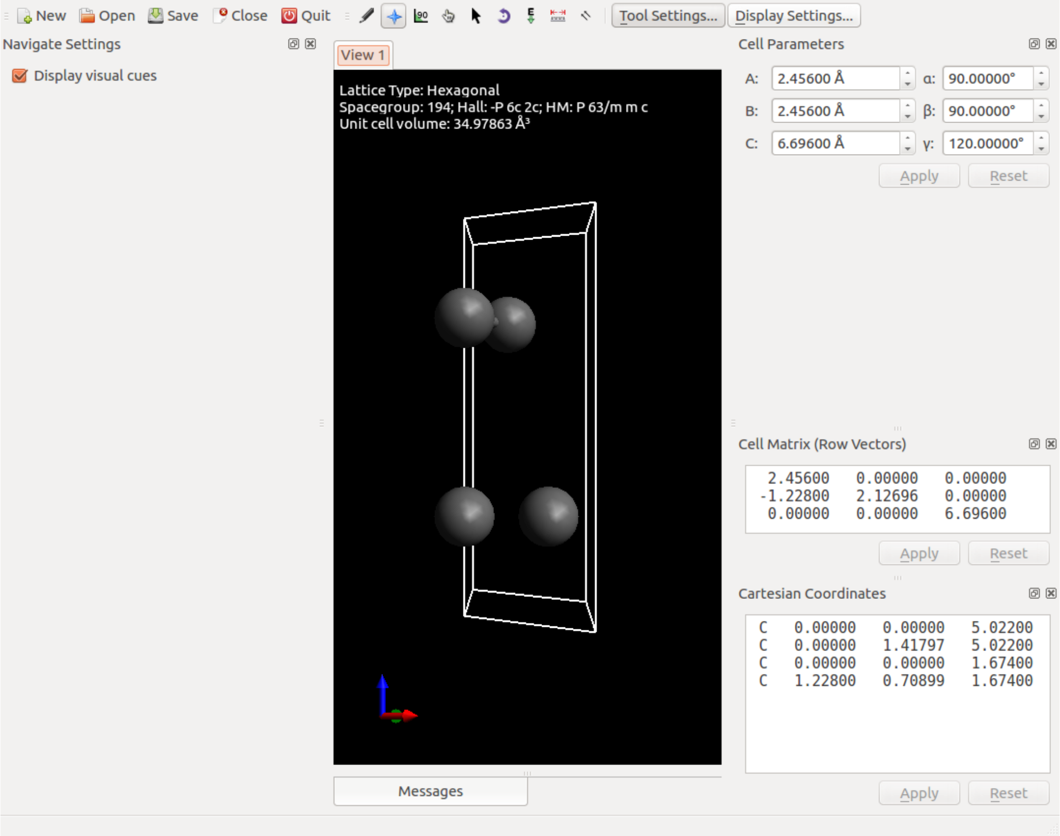
The special k-points on the x-axis are spaced out according to their distance in reciprocal space. The user may zoom in on the graph and right click it to translate it (although the x-axis labels may not remain true). The user may double click to return to the original orientation.

That concludes the diamond band structure exercise. Calculating the band structure of other materials can be done the same way. Be sure to perform a DOS calculation first to get an accurate Fermi level.

7 Projected Density of States Calculation (PDOS)

This section illustrates how to calculate the PDOS of graphite, which is described in the main text of the manuscript. As discussed in Section 2, a different set of parameters specifically parametrized for graphite was used in this calculation, whereas the default EHT parameters were employed for diamond. Therefore, in order to generate the graphs shown in this section one needs to follow the instructions in Section 2 to employ the same parameter set. PDOS calculations can provide information about the orbitals that are participating in bonding in a solid.

Open up the C-Graphite.cif file located in the "crystals"→"elements" directory that comes with AVOGADRO, and then click on "Reduce Cell (Primitive Reduce and Standardize)". This step is described fully at the beginning of Section 4. Once the cell has been reduced and standardized it should look as shown in Fig. 7.



☑ Display visual cues

```
Lattice Type: Hexagonal
Spacegroup: 194; Hall: -P 6c 2c; HM: P 63/m m c
Unit cell volume: 34.97863 Å³
```

Cell Parameters

A: 2.45600 Å α: 90.00000°
B: 2.45600 Å β: 90.00000°
C: 6.69600 Å γ: 120.00000°

Cell Matrix (Row Vectors)

```
 2.45600   0.00000   0.00000
-1.22800   2.12696   0.00000
 0.00000   0.00000   6.69600
```

Cartesian Coordinates

```
C   0.00000   0.00000   5.02200
C   0.00000   1.41797   5.02200
C   0.00000   0.00000   1.67400
C   1.22800   0.70899   1.67400
```

Figure 7: Standardized graphite crystal

In order to input the settings for our projected DOS calculation click on "Extensions"→"Yaehmop"→"Calculate Projected Density of States..." Other than the "Projections" option, the "Integrate PDOS?" option, and the "Display Total DOS?" option, the options are the same as those for the Total DOS described in Section 5. In this case, a "25 × 25 × 25" k-point grid is used. If this grid size causes YAeHMOP to fail, this number can be reduced (for example to "20 × 20 × 20").

In the "Projections" box, the user specifies the projections that they want calculated. Each projection line is divided up as follows:

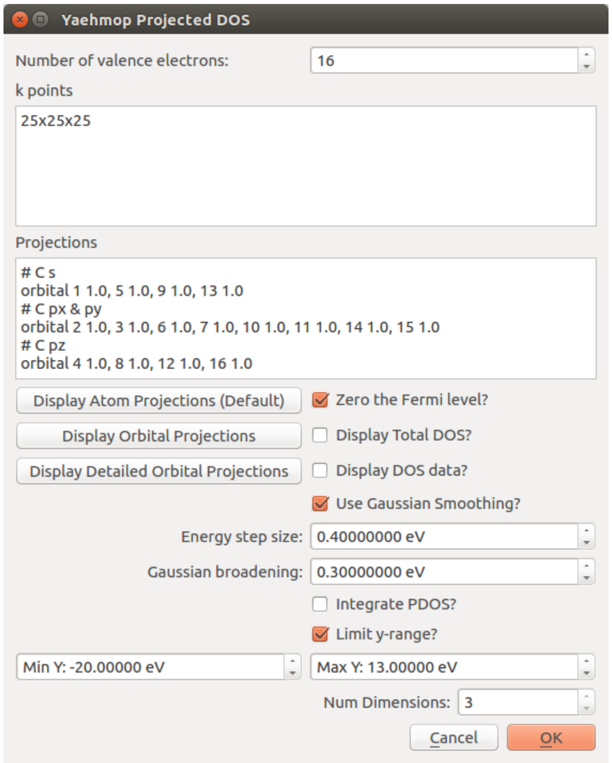
<type> <contrib1> <weight1>, <contrib2> <weight2>...

<type> can be either "atom" or "orbital", <contrib> is the atom's (or orbital's) number, and <weight> is the weight of that contributor. Fill in the dialog box as shown in Fig. 8. This can be done by copying and pasting the "Projections" text given below:

```
# C s
orbital 1 1.0, 5 1.0, 9 1.0, 13 1.0
# C px & py
orbital 2 1.0, 3 1.0, 6 1.0, 7 1.0, 10 1.0, 11 1.0, 14 1.0, 15 1.0
# C pz
orbital 4 1.0, 8 1.0, 12 1.0, 16 1.0
```

By default, the set of projections is generated for different atom types. Atoms are numbered with the same ordering shown at the bottom right of Fig. 7. The numbering for orbitals is a little bit more difficult to determine since different atom types have different numbers of orbitals.

To assist with obtaining the correct numbers of orbitals, the "Display Orbital Projections" and "Display Detailed Orbital Projections" buttons were added. When these buttons are pressed, the text in "Projections" will be replaced with a set of projections with the orbital numbers identified. "Display Orbital Projections" groups orbitals of the same type and from the same type of atom together. "Display Detailed Orbital Projections" only groups orbitals of the same type for each individual atom together. Note that this assumes that the only orbitals present are the ones that are occupied. YAeHMOP can employ unoccupied



Number of valence electrons: 16

k points

```
25x25x25
```

Projections

```
# C s
orbital 1 1.0, 5 1.0, 9 1.0, 13 1.0
# C px & py
orbital 2 1.0, 3 1.0, 6 1.0, 7 1.0, 10 1.0, 11 1.0, 14 1.0, 15 1.0
# C pz
orbital 4 1.0, 8 1.0, 12 1.0, 16 1.0
```

☑ Zero the Fermi level?
☐ Display Total DOS?
☐ Display DOS data?
☑ Use Gaussian Smoothing?
Energy step size: 0.40000000 eV
Gaussian broadening: 0.30000000 eV
☐ Integrate PDOS?
☑ Limit y-range?
Min Y: -20.00000 eV
Max Y: 13.00000 eV
Num Dimensions: 3

Figure 8: Projected DOS dialog box for graphite

orbitals as well if the user specifies a parameters file that has them. If that is the case, the numbering will be off, and thus the numbers must be determined manually by the user. The projections in Fig. 8 correctly separate the projections into s, (p_x, p_y), and p_z orbitals (p_x and p_y are identical). In addition, to assist with identifying the different curves in the plot, if a projection has a line immediately above it that begins with a “#”, that line will be used for the title in the legend.

When “Integrate PDOS?” is checked, the PDOS curves are integrated and plotted as well. The PDOS integrations have the same color as their corresponding PDOS curve, but they are thinner. “Display Total DOS?” plots the total DOS along with the PDOS. For the purpose of this exercise, it is left unchecked. Once all of the settings are correct, clicking “OK begins the calculation. When finished, the plot shown in Fig. 9 will appear, accompanied with the color legend shown in Fig. 10.

As the color legend states, the s orbitals are blue, the p_x and p_y orbitals are green, and the

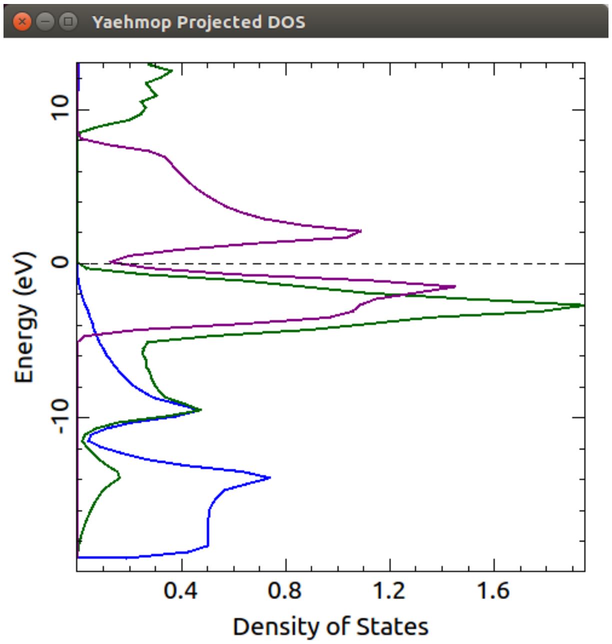
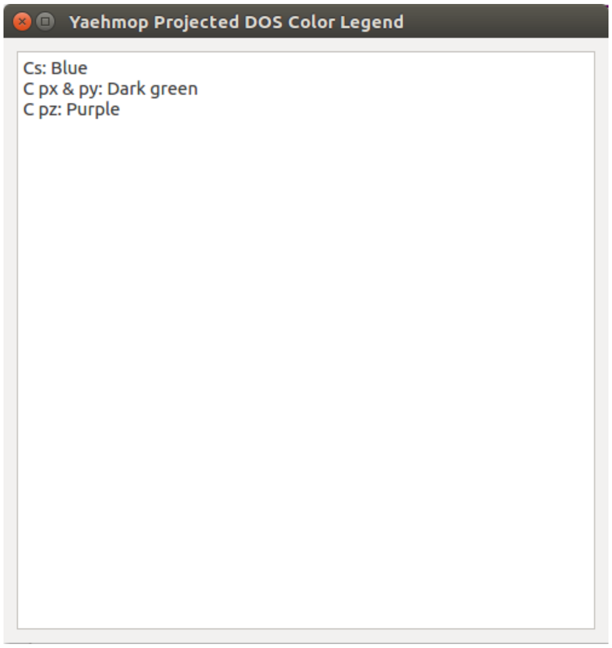


Figure 9: PDOS for graphite. Blue: s orbitals, dark green: p_x and p_y orbitals, purple: p_z orbitals.



Cs: Blue
C px & py: Dark green
C pz: Purple

Figure 10: Color legend for graphite PDOS

p_z orbitals are purple. Because the p_z orbitals do not hybridize with the s orbitals, they are higher in energy. The p_x and p_y orbitals, on the other hand, do hybridize with the s orbitals, and thus they extend down into the region below the p_z orbitals. The mixing between the p_x,

p_y orbitals and the s orbitals can be illustrated even further by performing another PDOS calculation using the same settings as in Fig. 8 except with the "Display DOS data?" and the "Integrate PDOS?" boxes checked. The resulting graph is given in Fig. 11. As the color legend indicates, the integration lines are the same color as the corresponding PDOS curves, but they are thinner. Upon examining the data in the "Yaehmop Projected DOS Results" dialog box that appears, one can see that at the Fermi level, the s orbitals integrate to about 4.94 electrons, the p_x, p_y orbitals integrate to about 7.01 electrons, and the p_z orbitals integrate to about 4.04 electrons. If there were no hybridization, we would expect the s orbitals to integrate to about 8 electrons and the p orbitals in total to integrate to about 8 electrons as well. However, since there is hybridization between the s and p_x, p_y orbitals, these numbers are different. Instead, we cay say there are about 12 sp^2 electrons (the s electrons plus the p_x, p_y electrons) and 4 p_z electrons. On a final note, Fig. 12 demonstrates that graphing a PDOS alongside a band structure plot can greatly assist in identifying the different bands.

That concludes the PDOS section. Remember one can use the "Display Orbital Projections" and "Display Detailed Orbital Projections" buttons to assist with numbering the orbitals correctly!

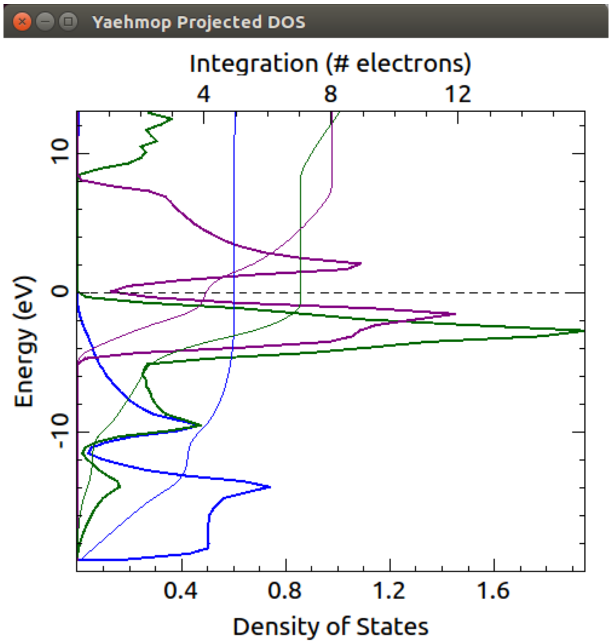


Figure 11: Example of PDOS integration for graphite

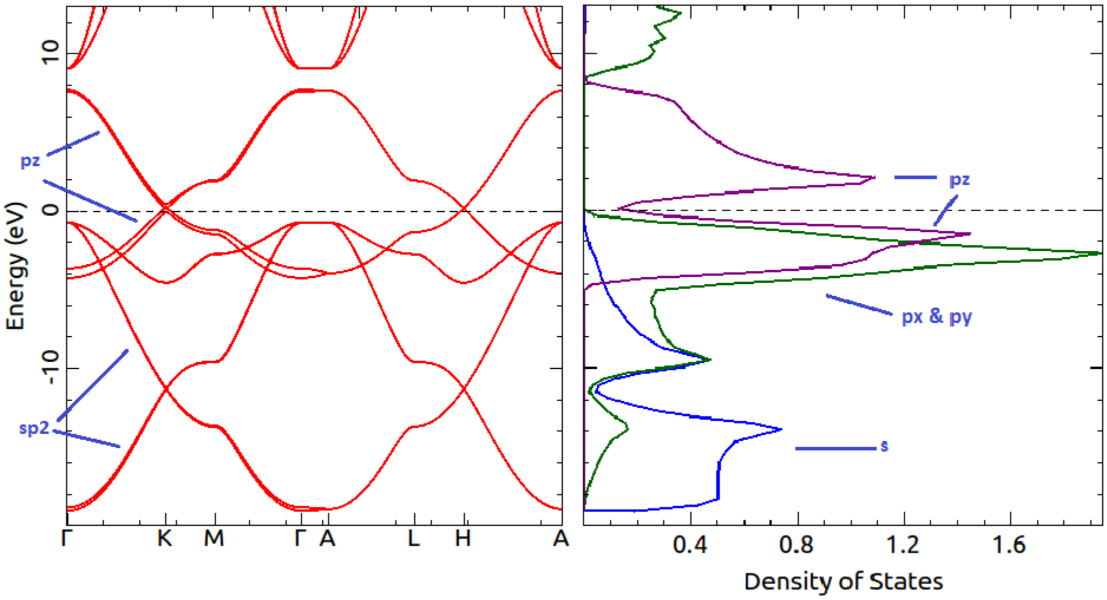


Figure 12: Comparison of the band structure and PDOS calculated for graphite. The PDOS plot can be used to help identify the character of the bands.

8 Crystal Orbital Overlap Population Calculation

The crystal orbital overlap population (COOP) is a density of states plot that has been weighted by the contribution to the overlap population. It can be used to identify the extent of bonding or antibonding interactions between orbitals on different atoms as a function of energy. The example used herein is introduced in Roald Hoffmann's book *Solids and Surfaces* [6] and a related article [7]. This example also demonstrates how to carry out calculations on a one-dimensional system.

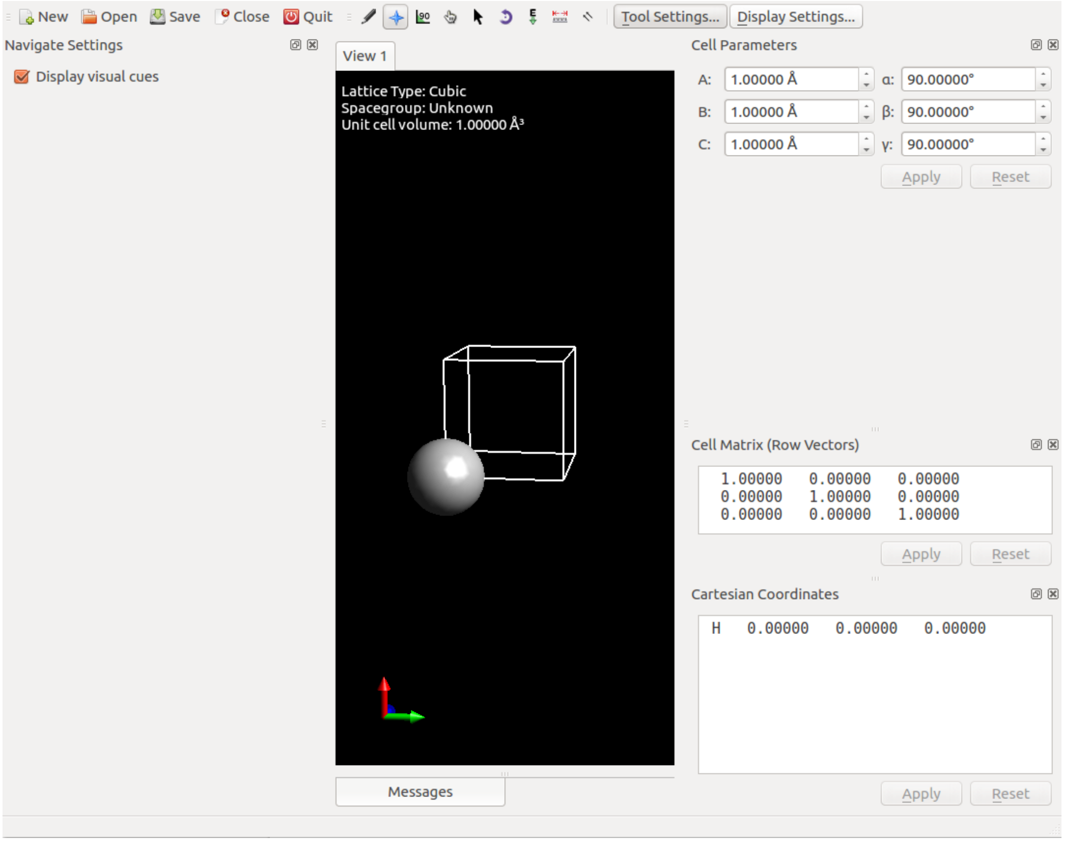
A linear hydrogen chain wherein all atoms are spaced 1 Å apart will be used in the calculations. To build a solid with this spacing in AVOGADRO click "Crystallography"→"Add Unit Cell". In the cell editor that appears on the right-hand side, set A, B, and C to all be 1, and set α, β, and γ to all be 90.0°. Then, in the coordinates section on the bottom right (it does not matter if it is Cartesian or if it is Fractional), type "H 0 0 0", then click "Apply". An image of a single hydrogen atom in the primitive unit cell will appear, as shown in Fig. 13. Note that this procedure yields a crystal that is periodic in three dimensions. Within YAeHMOP, however, we will specify that only a single direction (along the A lattice vector) is to be treated periodically. Thus, technically it does not matter what the B and C lattice vectors are. They are set to 1 Å for consistency.

To choose the settings for the COOP calculation click "Extensions"→"Yaehmop"→"Calculate Crystal COOP...", and fill in the dialog box as shown in Fig. 14. "Number of valence elections" only adjusts the Fermi level. It should automatically have been set to "1" because there is only one hydrogen atom in the unit cell. For systems that are ionic, this can be changed. Herein, keep the default value. The k-points box has already been described in the total DOS and PDOS sections. Since, in this example, a system that is 1-dimensional along the A lattice vector is employed, the k-points in the directions of the B and C vectors do not make a difference. That is why the k-points are set to be "300 × 1 × 1".

The "COOPs" section describes the COOP calculations to be performed. The format of each line is as follows:

<type> <coopNum> <contrib1> <contrib2> <a> <b> <c>

where <type> should either be "atom" or "orbital", depending on whether we are calculating a COOP between atoms or between orbitals (note that it may also be "h-atom" or



☑ Display visual cues

Lattice Type: Cubic
Spacegroup: Unknown
Unit cell volume: 1.00000 Å³

Cell Parameters

A: 1.00000 Å α: 90.00000°
B: 1.00000 Å β: 90.00000°
C: 1.00000 Å γ: 90.00000°

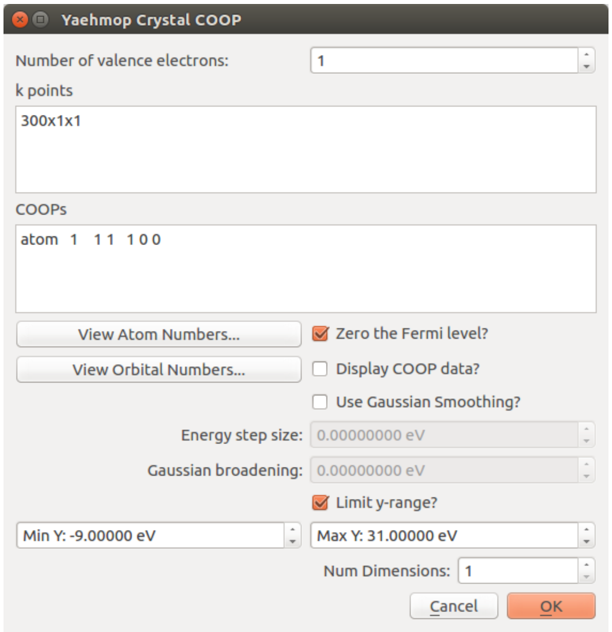
Cell Matrix (Row Vectors)

```
1.00000   0.00000   0.00000
0.00000   1.00000   0.00000
0.00000   0.00000   1.00000
```

Cartesian Coordinates

```
H   0.00000   0.00000   0.00000
```

Figure 13: Simple cubic unit cell containing one hydrogen atom, and a lattice length of 1 Å.



Number of valence electrons: 1

k points

```
300x1x1
```

COOPs

```
atom  1   1 1  1 0 0
```

☑ Zero the Fermi level?
☐ Display COOP data?
☐ Use Gaussian Smoothing?
Energy step size: 0.00000000 eV
Gaussian broadening: 0.00000000 eV
☑ Limit y-range?
Min Y: -9.00000 eV
Max Y: 31.00000 eV
Num Dimensions: 1

Figure 14: Crystal Orbital Overlap Population (COOP) dialog for neighboring hydrogen atoms

"h-orbital" if you wish to perform a Hamiltonian COOP calculation – also known as COHP [8]), <coopNum> is a specifier where all COOPs with the same <coopNum> will be averaged together to produce a single line, <contrib1> is either <atom1> or <orbital1> depending on the type, <contrib2> is either <atom2> or <orbital2> depending on the type, and <a> <b> <c> specify the cell that <contrib2> is to be in. So, for example, if <a> <b> <c> is "0 0 0", <contrib2> is in the unit cell. If <a> <b> <c> is "1 0 0", <contrib2> is in the cell neighboring the unit cell in the *A* direction.

In this case a COOP calculation between two hydrogen atoms in neighboring unit cells is being performed. This means that the COOP is between two hydrogen atoms that are adjacent to each other in the linear chain. Thus, <type> is "atom", the <coopNum> is 1 (it does not matter since we only have one COOP anyways), <contrib1> is atom number 1 (hydrogen), and <contrib2> is atom number 1 (hydrogen again) in the cell neighboring the unit cell in the *A* direction ("1 0 0" for <a> <b> <c>).

"View Atom Numbers..." displays a dialog that shows the user the atom numbers. This can be particularly helpful for larger systems. For this system, it isn't all that helpful since it is easy to figure out that the single atom would be atom number "1".

"View Orbital Numbers..." displays a dialog that shows the user the orbital numbers. This can also be particularly helpful for larger systems since the orbital numbers are not always easy to count out. For this system, it isn't all that helpful since there is only one orbital: the hydrogen *s* orbital. Note that if the user supplies a parameters file that has unoccupied orbitals in it, the orbital numbers displayed here may be off, and the user may need to determine them manually.

If the "Zero Fermi?" box is checked, all of the data will be adjusted so that the Fermi level is at zero. This can be very helpful to help determine which states are occupied and which are not, so herein the box is checked.

"Display COOP data?" will display the data so that it may be copied and pasted into a file for processing with external graphing software. The unadjusted Fermi level is printed first followed by the COOP values. Here, the box is left unchecked.

"Use Gaussian Smoothing?" fits the data to Gaussian functions to make it look significantly smoother. This can be very helpful in many situations. However, significant details will not be evident in this calculation using smoothing, so this box is left unchecked.

"Energy step size" may only be used if "Use Gaussian Smoothing?" is checked. The smaller this number is, the larger the number of points that will be created during smoothing. Thus, a smaller energy step size results in a more resolved graph. For most cases 0.1 eV is sufficient. Since smoothing is not performed here, this option does not matter.

"Gaussian broadening" may also only be used if "Use Gaussian Smoothing?" is checked. This number represents σ in the Gaussian distribution. The larger this number is, the smoother the graph will look. Since smoothing is not used here, this box is left unchecked.

If the "Limit y-range?" box is checked, the y-range of the displayed graph will be limited to be between "Min y" and "Max y". To help resolve features of the graph, check "Limit y-range?" and set "Min y" to be -9.0 eV and "Max y" to be 31.0 eV.

In order to make the hydrogen chain linear instead of 3-dimensional, the "Num Dimensions" at the bottom needs to be changed to "1". This makes the system periodic along the A lattice vector. Setting the number of dimensions to "2" ensures that the system is periodic along both the A and B lattice vectors.

Once all of the options match those in Fig. 14, clicking "OK generates the results, as shown in Fig. 15.

Note that a color legend should also appear as a separate dialog box. The legend prints out the title for each COOP (as they appear in the YAeHMOP output) and a color, the default being blue.

Positive values in the COOP indicate bonding overlap, and negative values in the COOP indicate anti-bonding overlap. Note also that there is a black vertical line at COOP $==$ 0 to help visualize whether the COOP is negative or not. Herein, the value at the lowest energy corresponds to all the hydrogen atoms being in phase with each other. As the energy of the

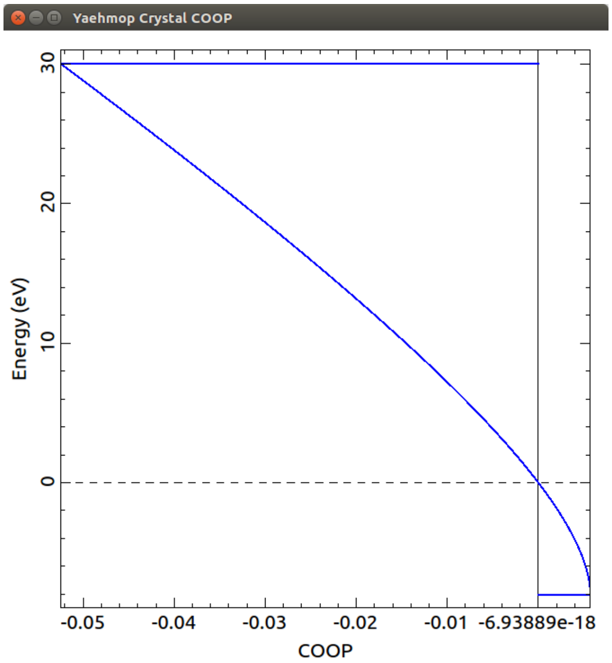
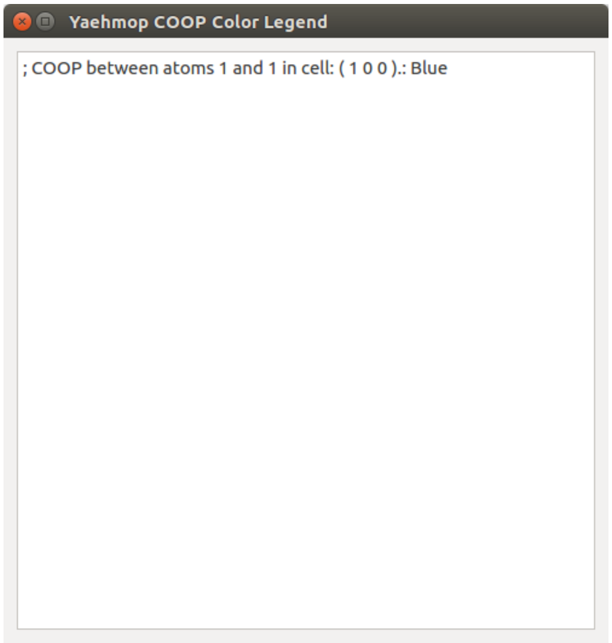


Figure 15: 1-dimensional hydrogen chain, COOP between adjacent hydrogen atoms



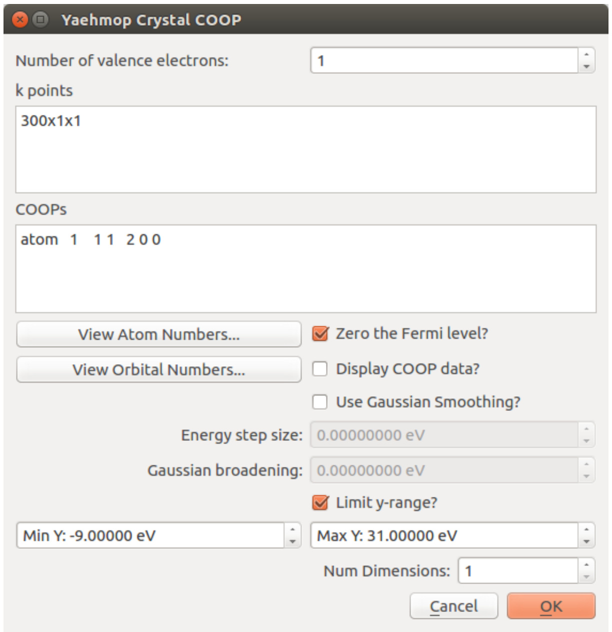
; COOP between atoms 1 and 1 in cell: (1 0 0).: Blue

Figure 16: 1-dimensional hydrogen chain, COOP legend

system increases, the interaction becomes more anti-bonding. This is shown schematically in Fig. 5 of the main text.

The COOP between second nearest neighbor hydrogen atoms can also be calculated.

This can be carried out by using the options in the dialog box illustrated in Fig. 17. Note that the only change is that <a> <b> <c> is now "2 0 0". This means that the second hydrogen atom is two cells away from the first in the A vector direction. This calculation yields the data given in Fig. 18.



Number of valence electrons: 1

k points

```
300x1x1
```

COOPs

```
atom  1   1 1  2 0 0
```

☑ Zero the Fermi level?

☐ Display COOP data?

☐ Use Gaussian Smoothing?

Energy step size: 0.00000000 eV

Gaussian broadening: 0.00000000 eV

☑ Limit y-range?

Min Y: -9.00000 eV

Max Y: 31.00000 eV

Num Dimensions: 1

Figure 17: Crystal Orbital Overlap Population (COOP) dialog for second nearest neighbor hydrogen atoms

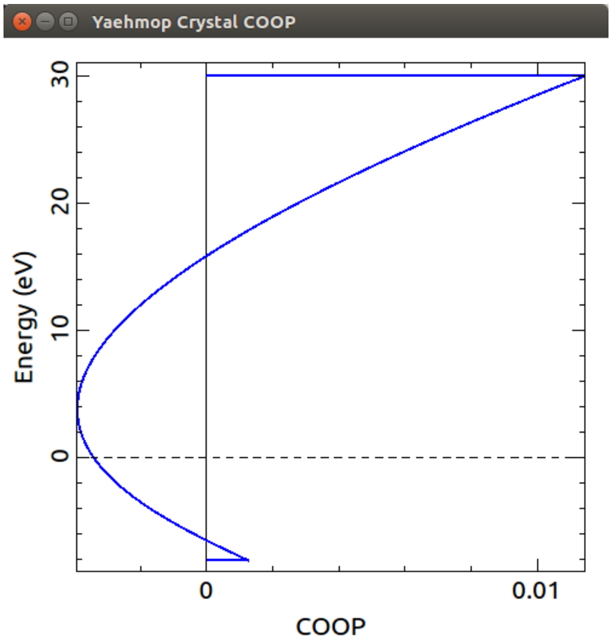


Figure 18: 1-dimensional hydrogen chain, COOP between second nearest neighbor hydrogen atoms

The second nearest neighbor hydrogen atoms are still all bonding at the minimum energy. As the energy increases, more of the second nearest neighbor hydrogen pairs become out of phase with each other, so anti-bonding interactions dominate. At the highest energy, however, every second nearest neighbor is in phase therefore yielding a bonding interaction.

This concludes the COOP section. Other COOPs can be performed in a similar way. The “View Atom Numbers...” and “View Orbital Numbers...” buttons can be used to see what the atom and orbital numbers are!

References

(1) 7-zip download page. https://sourceforge.net/projects/sevenzip/ (accessed Jul 2017).

(2) Fredrickson extended Hückel tuner. http://www.chem.wisc.edu/~danny/software/ehtuner/ (accessed Jul 2017).

(3) Stacey, T. E.; Fredrickson, D. C. Perceiving molecular themes in the structures and bonding of intermetallic phases: the role of Hückel theory in an ab initio era. *Dalton Trans.* **2012**, *41* (26), 7801–7813; DOI: 10.1039/c2dt30298e.

(4) Kresse, G.; Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47* (1), 558–561; DOI: 10.1103/physrevb.47.558.

(5) K-vectors and Brillouin zones of the space groups. http://www.cryst.ehu.es/cryst/get_kvec.html (accessed Jul 2017).

(6) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH Publishers: New York, 1988.

(7) Hoffmann, R. How Chemistry and Physics Meet in the Solid State. *Angew. Chem., Int. Ed. Engl.* **1987**, *26* (9), 846–878; DOI: 10.1002/anie.198708461.

(8) Dronskowski, R.; Bloechl, P. E. Crystal orbital Hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations. *J. Phys. Chem.* **1993**, *97* (33), 8617–8624; DOI: 10.1021/j100135a014.