

Calculating Band Structures for Organic Semiconductors

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Abstract

Band structures are very important in understanding the electronic structure of materials; as a result, a good methodology for finding the band structure for electronic materials is extremely important. Organic materials are focused on since their electronic structure is not as extensively researched. This research is purely computational, using molecular editing programs like Avogadro to model the organic semiconductors used and, Quantum Espresso to run all the calculations needed to find the band structure. Quantum Espresso uses density functional theory to calculate the wave functions and band structures for the organic semiconductors, and the program GNUplot is used to plot those band structures. Eight organic semiconductors are screened, while only three have had their band structure calculated. These three molecules are TTT-I3, TTF-TCNQ, and Pentacene. Their respective fermi energies are -0.88114 eV, -0.5583 eV, and 0.1890 eV. The band gaps for TTT-I3 and Pentacene that were calculated were 1.1507 eV and 0.141149 eV while TTF-TCNQ did not give a band gap in relation to the fermi energy. The results for the band structures were initially calculated over a symmetric wedge of the brillouin zone, so a new k-point path specific band structure was needed to be calculated in order to get a more accurate band gap for all the organic semiconductor molecules. Even though the band structures were initially not over a specific k-point path, the calculation still provided an estimate on the band gap. This research is a stepping stone for future work on calculating the band structure for organic semiconductors, and hopefully one day will provide a good methodology for calculating the band structure for any organic material.

Introduction

The main purpose of this research is to computationally calculate the band structure of organic semiconductor crystals. The process of this research was to calculate the band structures of the organic semiconductor crystals and then compare the computed values to experimentally verified values in order to find out how accurate the computational methodology used was. This research was done using the OSU HPCC (High Performance Computing Center), the programs Avogadro [1], Quantum Espresso [2] and GNUplot. This research sheds light on the accuracy of various density functional theory (DFT) functionals used to calculate the band structure of organic semiconductor crystals.

To compute accurate band structure's for organic semiconductor crystals, an accurate representation of the crystal lattice is needed. For basic crystals, the ordered arrangement of atoms in a solid can be described by using a lattice and a basis. A lattice is a spatially periodic array of points, and a basis is an atom or a group of atoms that will be positioned at each lattice point [3]. In the case for the organic semiconductor crystals used in this project, the basis will be an organic semiconductor molecule or charge-transfer salt. Each lattice point can be represented as a linear combination of a set of primitive lattice vectors as in equation 1. Where a represents lattice vectors and n are integer values.

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (1)$$

The volume bounded by the three primitive lattice vectors is the unit cell of the crystal in real space. The entire crystal can be built from this unit cell by stacking them together. Another type of unit cell that is commonly used is the *Wigner-Seitz* unit cell, which is created by drawing vectors starting at the origin to each of the nearest neighboring lattice points, and then bisecting the vectors normal to each vector [3]. In the *Wigner-Seitz* unit cell, any location within the unit cell is closer to the origin lattice point than it is to any other lattice point. These unit cells define the real space periodicity of a crystal; however, for solid state physics and calculating the band structure of a crystal the k-space (momentum space) lattice is needed. The primitive lattice vectors can be translated into k-space reciprocal lattice vectors as shown in below.

$$\begin{aligned}
 \mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\
 \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)} \\
 \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} \\
 \mathbf{G} &= n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \quad (2)
 \end{aligned}$$

The vectors $\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$ are a set of basis vectors for k-space. Any point in reciprocal lattice space can be defined in equation 2. Both the real space lattice and the reciprocal lattice are important in defining the crystal, where the real space lattice may determine the physics structure of the crystal the k-space lattice can determine the possible x-ray reflections created through diffraction [4]. The Brillouin zone is defined as the *Wigner-Seitz* cell of the reciprocal lattice [4]. The Brillouin zone and its boundaries are very important in dealing with periodic potentials and as such is very important in computing accurate band structures.

Band theory is extremely important in understanding solids and their electrical, thermal and optical properties. The band structure and band gap of a solid is notably very important in determining if a solid is an insulator, metal or semiconductor. Every solid contains electrons, the band structure is a visual representation of the energies of the electrons in a solid. The electrons in a solid's crystal are arranged in bands, of these bands, the valence and conduction bands help identify the band gap. The valence band consists of the highest occupied crystal orbital while the conduction band makes up the lowest unoccupied crystal orbital. Between the valence band and the conduction band is a space where no wavelike electron orbitals can exist, this area is called the band gap [4]. The band structure and band gap can be used to compute many electronic and thermal properties of a solid, therefore a good computational method to find the band structure of solids would be very helpful in future research on organic semiconductors.

To find the band structure computationally we use the program Quantum Espresso [2], which uses density functional theory (DFT) calculations to find both the wave functions and

band structures. Density functional theory is an electronic structure technique that was created by Hohenberg and Kohn in 1964, and then formulated into a methodology by Kohn and Sham in the following year [3]. Density function theory is used to solve many-body systems with the time independent Schrodinger equation. With DFT, Hohenburg and Kohn proved that for any system of interacting particles in an external potential, the ground state particle density determines the Hamiltonian [3]. This implies that all the properties of this system can be determined with the density function; likewise, they also showed that there must be an energy functional in terms of the density. The approach used to solve for this energy functional is called the Kohn-Sham approach. This approach assumes that the interacting density is the same for a particular non-interacting system. Due to the effects of the non-interacting system, all the complexities of the interacting system are combined into an exchange-correlation functional [3]. Therefore, the exchange-correlation functional can be approximated to solve for the solution for the non-interacting system, which then can be approximated for the real interacting system. There are two different DFT methods using the Kohn-Sham approach. Local density approximation (LDA) assumes the exchange-correlation energy depends on the local density, while generalized gradient approximation allows the exchange-correlation energy to depend on the gradient of the local density [3].

Molecular Database

The scope of this research focuses on optimizing organic semiconductor crystals computationally in order to calculate their band structures. The first step of this research was to create a database of well documented and experimentally researched organic semiconductor crystals. The main properties of the semiconductor crystals that we were looking for were the crystal parameters and the bands gaps. The crystal parameters are denoted as a , b , c , α , β , and γ . The parameters a , b and c represent the lengths of the x, y and z edges of the unit cell of the crystal, while α , β , and γ represent the angles between any two crystal parameter a , b or c . The angle α represents the angle between b and c , while β is the angle between a and c , and γ is the angle between a and b . With these six crystal parameters (Table 1) and the chemical diagrams (Figure 1) for the organic semiconductors, the unit cells for our crystal can be made with the program Avogadro [1].

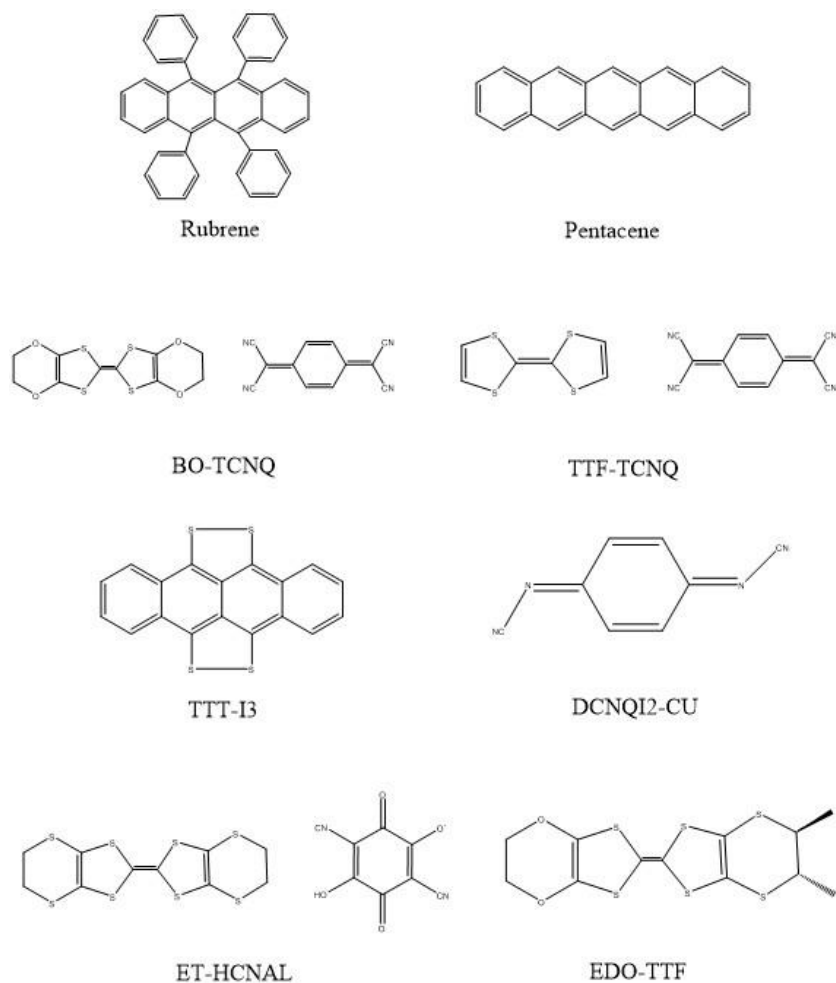


Figure 1. List of organic semiconductor molecules used in research [5-13]

<u>Molecule</u>	<u>A</u>	<u>B</u>	<u>C</u>	γ	β	α	<u>Cos(γ)</u>	<u>Cos(β)</u>	<u>Cos(α)</u>	<u>Lattice system</u>
TTF-TCNQ	12.298	3.819	18.468	90	104.46	90	0	-0.2497	0	Monoclinic
TTT-I3	18.394	4.926	18.391	90	90	90	0	0	0	Orthorhombic
Pentacene	5.93	7.56	15.65	89.8	93.3	98.6	0.00349	-0.05756	-0.14953	Triclinic
Rubrene	26.86	7.19	14.43	90	90	90	0	0	0	Orthorhombic
ET-HCNAL	7.606	6.773	34.531	90	93.12	90	0	-0.054427	0	Monoclinic
BO-TCNQ	23.897	7.327	7.053	90	93.37	90	0	-0.05878	0	Monoclinic
DCNQI2-CU	21.566	21.566	3.801	90	90	90	0	0	0	Tetragonal
EDO-TTF	7.4048	7.4048	67.995	90	90	90	0	0	0	Tetragonal

Table 1. The lengths of a , b and c are measured in angstroms, while the angles γ , β and α are measured in degrees [5-13]

Computational Details

Table 1 represents the crystal parameters of the organic semiconductors needed to actually model these crystals. Once the organic semiconductors are created through Avogadro and aligned accordingly with their crystal parameters, the next step is to run a molecular dynamics force field calculation. The force fields MMFF94 and MMFF94s are used in this project, since they work well with organic compounds [14]. After the molecular mechanics force field calculation converges, the unit cell for our organic semiconductor crystal will be geometrically optimized according to molecular mechanics. However, now the geometry must be optimized using DFT calculations via Quantum Espresso [2]. From the Avogadro file that we have the unit cell for our organic semiconductor, we will need to create an “.xyz” file for our input script for Quantum Espresso. This gives us the coordinates of all the atoms in our unit cell.

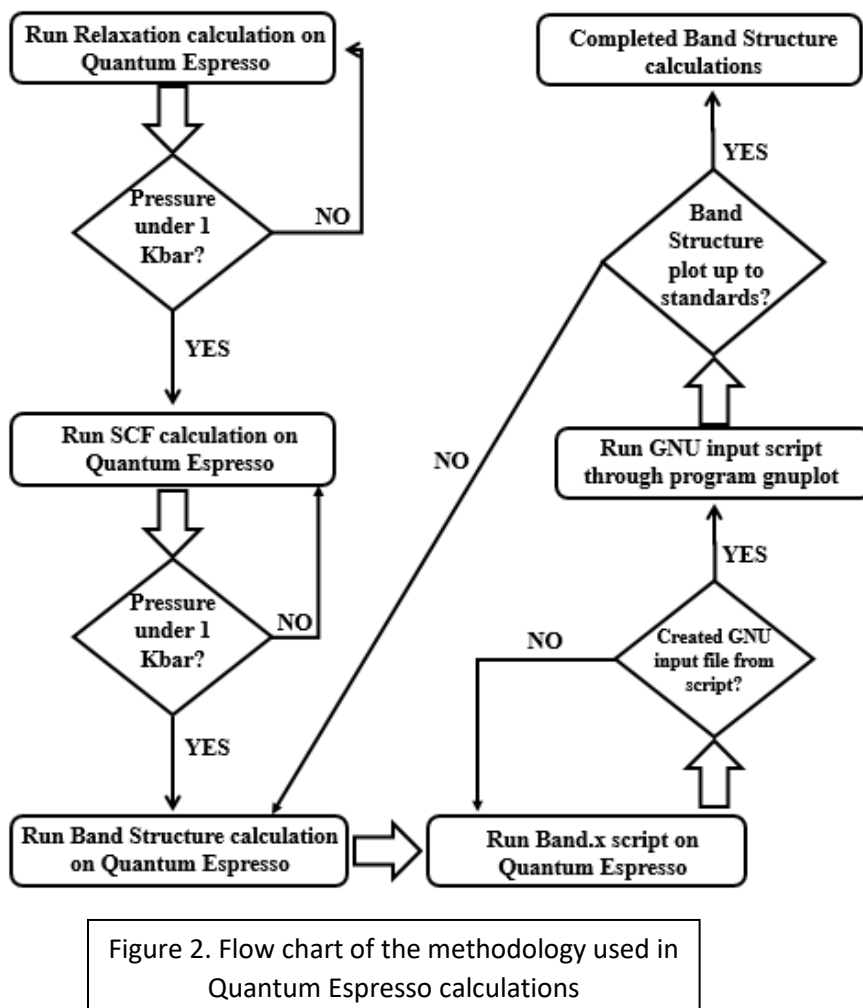
Using the xyz coordinates taken from Avogadro, a geometry relaxation calculation is performed at the DFT level using Quantum Espresso. This calculation determines the forces acting on the unit cell of the molecule represented in the xyz coordinates, and then uses them to find the optimal geometry of the molecule more accurately than what was obtained at the molecular dynamics level. The xyz coordinates of the unit cell are needed to specify what exactly is being calculated; however, there are many other conditions that need to be specified in order to accurately run the geometry optimization calculation. A sample input script for the semiconductor TTT-I3 is given in appendix A. The overall structure of the input script for the

Quantum Espresso calculations done in this research is constant throughout, the format of the script used in the relaxation calculation can be used for all the other calculations. There are eight sections to the input script that are needed to be optimized for each calculation. The first section is control, where details on the how the calculation is run is specified. For control, the relax calculation must be specified as well as the pseudo directory and output directory. The pseudopotentials replace the coulomb potentials in the molecules with modified potentials for the DFT calculations. Here PBE pseudopotentials were used from the Borunda group directory. The output directory is a temporary directory where output files from the calculation are stored, here the output directory is denoted tmp. The conditions wf_collect, tstress, and tprnfor must be specified as true (as seen in appendix A). wf_collect as true allows for the calculation to collect wavefunctions from all processes in the calculation and store them in the output directory. The conditions tstress and tprnfor as true allow for the calculation to calculate both the stress and the forces on the unit cell, which are important in optimizing the geometry. The final condition for the control section is the force convergence threshold, in which 0.002 a.u. is specified.

The next section is system, which specifies details on the system that is being calculated on, in particular the crystal parameters of the unit cell. Here both the lattice system is the first condition that would need to be defined, every lattice system is defined as a number to be listed under ibrav. After specifying the lattice system the crystal parameters are needed, these are listed as a, b, c, and the cosines of gamma, beta, and alpha. This specifies the structure of the crystal, and then the number of atoms and the number of different types of atoms are needed (nat and ntyp). The kinetic energy cutoffs for both the wavefunctions and the charge density are also needed to be defined, here ecutwfc is denoted as 60 Rydberg and ecutrho is denoted as 240 Rydberg. The final specifications for the system section of the input file is occupations, which is defined as smearing, which is a method for finding the fermi surface of a system. Here the Methfessel-Paxton method (m-p) method of smearing is used, and degauss is defined as the value of Gaussian spreading in the brillouin zone. The sections electrons, ions and cell variables were defined accordingly as in appendix A. These values were chosen due to them being the best values for the calculations needed in this research. The section atomic species is where the pseudopotentials are defined, and the following section is the atomic positions, where the xyz coordinates of the unit cell are listed. The final section denotes the K-points, for the relaxation calculation automatic k-points are used. Detailed k-point values are not needed till band structure calculations.

Once the input script for Quantum Espresso is created, this script can be used as a template for input scripts for SCF and band structure calculations. With the input script created, the calculations with Quantum Espresso can be started. The entire methodology used on Quantum Espresso is denoted in figure 2. For the relaxation calculations, the calculation is run over and over until the pressure acting on the unit cell for the semiconductor molecule used is under 1 Kbar. When the pressure acting on the unit cell is under 1 Kbar, the unit cell of the crystal is closest to its ground state, which is what is needed for accurate band structure calculations. After an initial calculation, if the pressure is not under 1 Kbar, the calculation is

repeated with slightly altered crystal parameter values until the pressure reaches the needed value.



After the relaxation calculation is completed, and the pressure is under 1 Kbar, the next step is to run a SCF (Self-Consistent Field) calculation. The SCF calculations is an iterative method of solving for the wave function of the molecule/semiconductor. The SCF method approximates a Hamiltonian, and then solves the Schrodinger equation for that Hamiltonian and repeats this process till all the results converge [2]. Here the final xyz coordinates from the relaxation calculation output file is used, and the sections ions and cell can be ignored. After changing the calculation type to SCF, all other properties of the input script can be left the same. After running the SCF calculation, the pressure acting on the unit cell should automatically be under 1 Kbar since the geometry has already been optimized. If so, then the wave functions will be stored in the out-directory for use when the band structure calculations are started.

After completing the SCF calculation, the next step is to start the band structure calculation. For the input script for the band structure calculation, the sections ions and cell can

be ignored like in the SCF calculation. In the control section, the terms “nbnd” and “nosym” must be added. The term nbnd represents the number of bands, this number is dependent on the number of valence electrons in the semiconductor unit cell that is being used. The number of bands is half the number of valence electrons in the unit cell. The term nosym is asking if symmetry should be used in this calculation or not. In these band structure calculations we define this term as false, symmetry is used here. For the band structure calculations, the k-point path must be specified in order to find an accurate band structure. Depending on the path needed, the k-points cannot be denoted as automatic anymore, but each point on the k-point path must be defined using the reciprocal lattice vectors of the unit cell. Once the k-point path is defined, the last step is to make sure that the out-directory from the SCF calculation is present in the directory of the band structure calculation. This is needed because the out-directory contains the wave functions needed for a band structure calculation. After completing the band structure calculation, the next step is to take the output file/out-directory and run a band.x script. This takes the output file and out-directory from the band structure calculation and creates a “.gnu” file for the band structure. Using this “.gnu” file, the program GNUplot is used to create the actual band structure graphs.

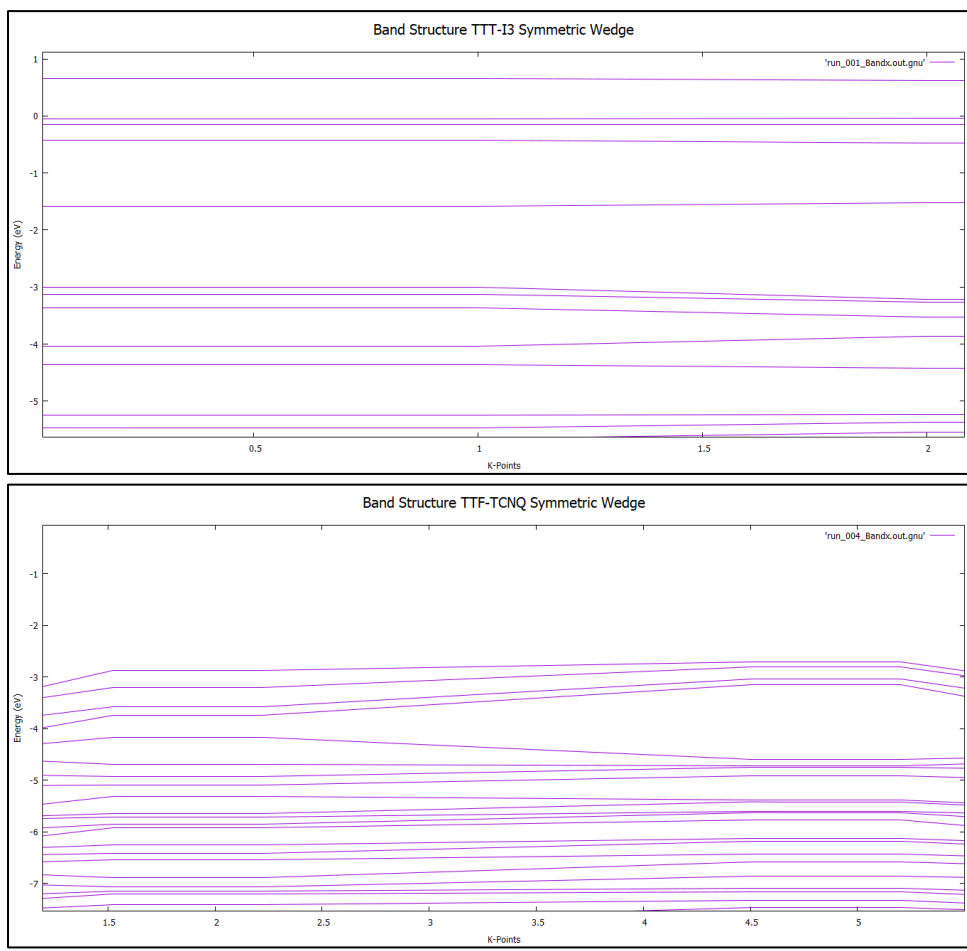
Results and discussion

Out of the eight organic semiconductors that were studied in this project, three made it through the entire methodology depicted in figure 2. Those three semiconductors were TTT-I3, TTF-TCNQ and Pentacene. The other five organic semiconductors are all still on the geometry relaxation phase. The difference in the amount of computational time needed for the relaxation of the five organic semiconductors still running and the three that finished may be due to the more complex nature of the unit cells of Rubrene, BO-TCNQ, EDO-TTF, DNCQI2-CU and ET-HCNAL. If the unit cell of a crystal in Quantum Espresso has a large number of atoms and many different types of atoms, the calculations take much more time due to there being more forces to calculate and more pseudopotentials to integrate into the calculations. Rubrene, BO-TCNQ, EDO-TTF, DNCQI2-CU and ET-HCNAL have all relaxed down to single digit pressure values; however, these values are still not under 1 Kbar. If these crystals continue to have trouble converging to a pressure below 1 Kbar, an alternate method for relaxation may need to be implemented. A variable-cell relaxation step could improve make the relaxation more accurate, this “VC-relax” calculation would go before the regular “relax” calculation. VC-relax would make the finding the initial unit-cell parameters much easier; however, it could also add more calculation time if the unit-cell parameters were not the issue.

The semiconductors TTT-I3, TTF-TCNQ, and Pentacene all completed the entire methodology depicted in figure 2. However, the initial band structure calculations were done over a symmetric wedge (figure 4) of the brillouin zone instead of on a specified path through the brillouin zone as in the literature. This was done by changing the calculation type on the input script to “bands” and leaving the k-points as “automatic”. This method did produce band

structures; however, these band structures do not depict the correct k-point path that is needed. The bands created through this method is depicted in figure 3.

The fermi energies of each semiconductor is needed to calculate the band gap. The fermi energy is calculated through Quantum Espresso in the SCF wave function calculation, so the fermi energies are not dependent on the band structure. The fermi energies for TTT-I3, TTF-TCNQ and Pentacene were -0.88114 eV, -0.5583 eV and 0.1890 eV respectively. The band gaps of the organic semiconductors from the initial (symmetric wedge) approach were calculated with the fermi energies. The band gaps for TTT-I3 and Pentacene were 1.1507 eV and 0.141149 eV. The band gap for TTF-TCNQ was unable to be calculated because the fermi energy was at a higher energy level than all the bands calculated through Quantum Espresso. This means that it was impossible to find the energy gap between the conduction and the valence band with the information provided.



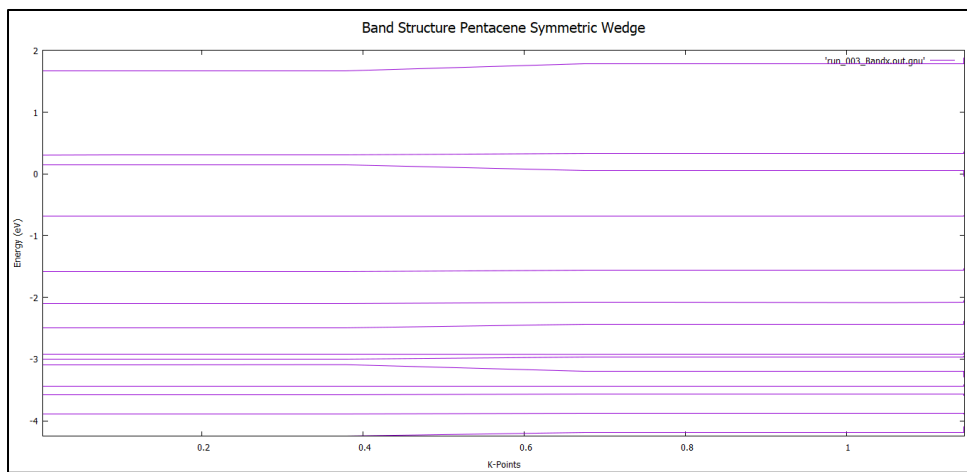


Figure 3. Band Structures for TTT-I3, TTF-TCNQ and Pentacene using the symmetric wedge of the brillouin zone

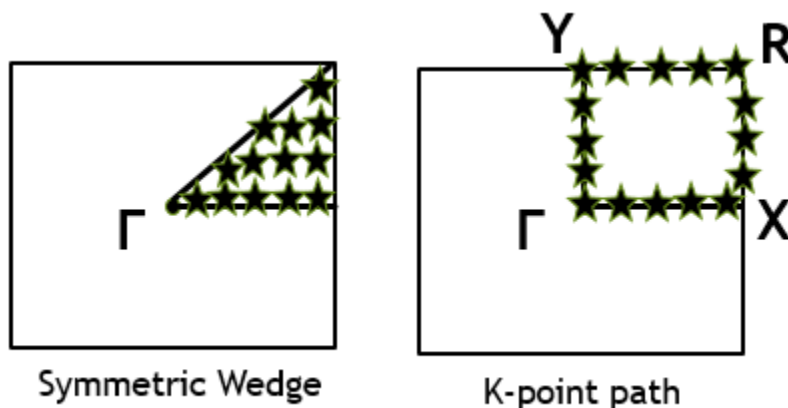


Figure 4. 2D depiction of the symmetric wedge versus the k-point path method for calculating the band structure

Even though the band gaps from the band structures calculated through the symmetric wedge method may not give an accurate representation of the experimentally verified band structure of the organic semiconductors, they can give us an estimate of the band gaps. The band gap is found by taking the fermi energy, and then finding the bands above and below and taking the energy difference between the highest and lowest point of each band. With most band structures, the bands would not be as horizontal as they are in the band structures in figure 3. This is why a more precise method of calculating the band gap is needed. However, with TTF-TCNQ and Pentacene, their band structures and the fermi energy for Pentacene show that there might be issues with the actual unit cell of each of these organic semiconductors. Pentacene's

fermi energy was positive, which very unusual for a semiconductor and then there was the issue of being unable to find the band gap for TTF-TCNQ. For these two semiconductors, the next step would be to go back to the relaxation phase of the methodology in figure 2. In order to realign the unit cell and make sure all the initial conditions for relaxation are correct and in line with the experimental values.

For TTT-I3, there did not seem to be any issues with the actual unit cell for the organic semiconductor. For this semiconductor, the band structure was re-calculated using the “tpiba” method for the k-points. The “tpiba” method reads the k-points in cartesian coordinates in units of $2\pi/a$. Knowing that TTT-I3 is orthorhombic, the specific k-point path can be found using a symmetry k-point table. For this research the k-point table for the orthorhombic TTT-I3 is denoted in table 2. Since the lattice system is orthorhombic, the reciprocal lattice vectors are in the x, y and z directions in the cartesian plane.

xb_1	xb_2	xb_3	Symmetric points	xb_1	xb_2	xb_3	Symmetric points
0	0	0	Γ	$\frac{1}{2}$	0	$\frac{1}{2}$	U
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	R	$\frac{1}{2}$	0	0	X
$\frac{1}{2}$	$\frac{1}{2}$	0	S	0	$\frac{1}{2}$	0	Y
0	$\frac{1}{2}$	$\frac{1}{2}$	T	0	0	$\frac{1}{2}$	Z

Table 2. Symmetric k-point table for an orthorhombic lattice crystal structure [15]

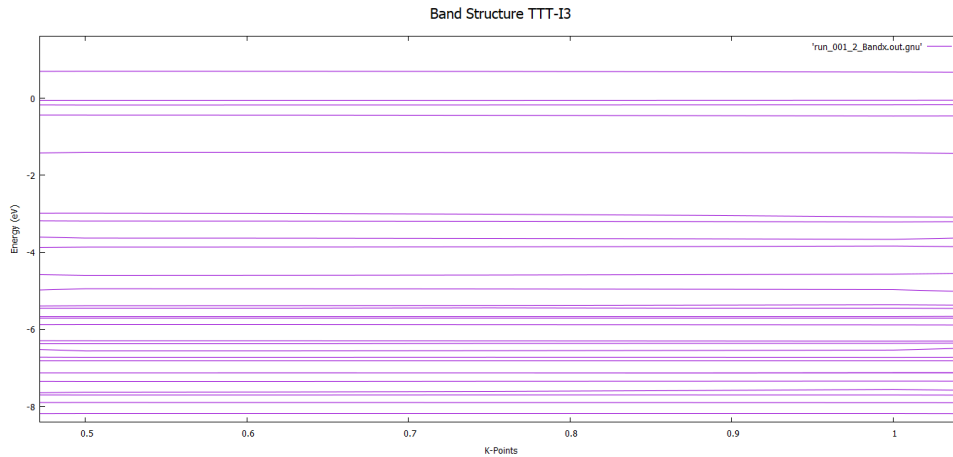


Figure 4. Band Structure of TTT-I3 using the tpiba k-point method

The band structure calculated from the “tpiba” k-point method is shown in figure 4. Here the band gap was 0.974854 eV. The path taken was Γ -X-S-Y- Γ , and between each symmetric k-point, five points in between each were also calculated in order to add accuracy to the band structure calculation. Here the band gap value differs greatly from the previous calculation method; however, the structure of the bands are still very horizontal compared to the parabolic curves that are seen in most band structures. The next steps to be taken would be to recalculate the band structure for TTT-I3 and attempt a different method than “tpiba”. One other method would be to calculate the reciprocal lattice vectors by hand and then plot a path with those vectors as a basis. One other tool that can be used in future work are CIFs (crystallographic Information Files). Papers which specify the CIF file used in their research give a much more accurate representation on the crystal structure of the molecule/semiconductor than papers which do not specify the CIF. Using the CIF, the unit cell of the organic semiconductor will be automatically created and could therefore cut the computational time of the calculation by a large amount.

Conclusion

There is still a lot of future work to do done, in particular with finding a better method for calculating band structures as well as further work on finishing relaxation runs for the five molecules that did not finish. The band structures that were calculated in this project are not good for these type of organic semiconductors. The bands were very flat, flat bands mean there is not much movement in the electrons, meaning very little electrical conduction. This cannot be the case for these molecules, since they are well known thermoelectric materials, which have high electrical conductivity. This means that future research will need to start with a better band structure calculations. This research has allowed me to explore how crystal structures work and how to model crystal structures using computational techniques and DFT. With a good computational methodology for finding the band structure for organic materials many other types of organic semiconductors can also be screened. Being able to calculate the band structure for any organic semiconductor without having to physically create the semiconductor would save future researchers a lot of time, and thus help further research on organic materials. The research done so far is a good stepping stone for that ultimate goal of getting a good methodology for calculating the band structure for organic semiconductors.

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Appendix A:

Sample Quantum Espresso input script for the semiconductor TTT-I3.

```
&CONTROL
  calculation = 'relax',
  wf_collect = .true.,
  prefix = 'TTT_relax',
  forc_conv_thr = 0.00200,
  tstress = .true.
  tprnfor = .true.

  pseudo_dir='/project01/borundagroup/local_pse
  udos/PBE/scalar_relativistic/ONCV'

  outdir = 'tmp/',
/

&system
 ibrav = 9,
  a = 18.394,
  b = 4.926,
  c = 18.391,
  cosab = 0,
  cosac = 0,
  cosbc = 0,
  nat = 31,
  ntyp = 4,
  ecutwfc = 60.0,
  ecutrho = 240.0,
  occupations = "smearing",
  smearing = "m-p",
  degauss = 0.05,

/

&electrons
  mixing_beta = 0.2,
  conv_thr = 1.0d-6
/

&IONS
  upscale = 100,
/

&CELL
  press = 1.0,
/

ATOMIC_SPECIES
C 12.0107 C_ONCV_PBE-1.0.upf
H 1.0079 H_ONCV_PBE-1.0.upf
S 32.059 S_ONCV_PBE-1.0.upf
I 126.904 I_ONCV_PBE-1.0.upf
ATOMIC_POSITIONS {angstrom}
/

K_POINTS {automatic}
```