# Energy Band Calculation of Molecular Conductors 

(For windows)
Revised April 2024
Examples of scal.dat and tbmap.dat are replaced using the current files.

## 1. Introduction

This is an instruction manual for computer program of energy band calculation particularly designed for molecular conductors. The source is coded by FORTRAN, so the program is executable on any computer system which has FORTRAN compiler. As for the theoretical background of this program, consult Ref.1.

1) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Bull. Chem. Soc. Jpn., 57, 627 (1984).

Download the following files in the same folder of your PC.
trcifg3.exe extdh.exe extdh.dat scal.exe scal.dat tbmap.exe tbmap.dat fermi.plt
Using the right bottom of your mouse, you can download the xxx.dat files. There are several versions; for example, extdhg3.exe is the newest version of extdh.exe. The program names are variable, but the program always tries to read the above input files.

## 2. Convert Atomic Coordinates

(1) When the crystal structure has been known, the atomic coordinates are included in the cif file. In old ACS journals, we can get the cif files from the supporting information. For other journals, copy the paper doi number to the CCDC site
https://www.ccdc.cam.ac.uk/structures/?
and you can get the cif file.
(2) To display the crystal structure, use Mercury.
https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/
(3) To prepare the band calculation, open the cif file using a text editor (the right bottom of your mouse). Atomic coordinates usually appear following the statement.
atom_site_disorder_group
Typical format is
C1 C 0.1478(4) 0.52700(6) 0.45247(6) 0.0106(3) Uani 11 d . . . . .
This line indicates atom name, atom species, $x, y, z$ fractional coordinates (errors in the parentheses), temperature factor and so on. It is recommended to change the atoms in the order of the atom species: sulfur, carbon, hydrogen.
(4) Save the cif file as atom.cif.
(5) If the molecule is located on an inversion center at $(0.5,0.0,0.5)$, we can make the whole coordinates by applying the symmetry operation ( $1-x,-y, 1-z$ ). In that case, change trcif.dat (you can download) as

$$
\begin{array}{llll}
11.0 & 0.0 & 1.0 & (\mathrm{I} 5,3 \mathrm{~F} 5.0)
\end{array}
$$

(6) Run trcifg3.exe by double clicking the file, and at.dat is generated. This file contains the lattice constants and atomic coordinates that can be used in extdh.dat and scal.dat.
(7) (In case of error) The format of cif is variable. When the format is largely different, trcif fails. It sometimes happens that the atom species ("C" in the example in (3)) are missing. If the atom species are added, trcif may be successful. When the digits of the coordinates are too small or too large, trcif may fail. The same happens for the lattice constants; in such a case, it may be easier to copy the numbers directly from the cif file.

## 3. Extended Hückel Molecular Orbital Calculation: EXTDH

As for each crystallographically independent molecule, calculate the molecular orbitals by the extended Hückel method.
(1) It is recommended to make a table as follows.

BEDT-TTF

|  | Atoms | Electrons |  | Orbitals |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| S | 8 | 6 | 48 | 9 | 72 |
| C | 10 | 4 | 40 | 4 | 40 |
| H | 8 | 1 | 8 | 1 | 8 |
|  | 26 |  | 96 |  | 120 |

A BEDT-TTF molecule contains eight sulfur, ten carbon, and eight hydrogen atoms. A sulfur atom has six valence electrons so that the eight $S$ generates $6 \times 8=48$ valence electrons. Similarly C and H give up 40 and 8 electrons, thereby a molecule has 96 valence electrons. For sulfur we will make one 3 s , three 3 p (namely $3 p_{x}, 3 p_{y}$, and $3 \mathrm{p}_{\mathrm{z}}$ ), and five 3 d orbitals, then there are $1+3+5=9$ orbitals on each S atom. A carbon has $2 \mathrm{~s}+2 \mathrm{p}=4$ orbitals, and a hydrogen has one 1 s orbital. Therefore, the total number of orbitals are 120. We will use these numbers later.
(2) The content of extdh.dat is as follows.


| 2 | -0.0486 | -0.3972 | 0.6993 | C6 |
| ---: | ---: | ---: | ---: | :--- |
| 2 | 0.6312 | 0.0229 | 0.2263 | C 7 |
| 2 | 0.4268 | 0.0233 | 0.1917 | C |
| 2 | 0.0400 | -0.4922 | 0.8821 | C |
| 2 | -0.1860 | -0.5212 | 0.8527 | C 10 |
| 3 | 0.7181 | 0.0276 | 0.1747 | H 1 |
| 3 | 0.7024 | 0.1220 | 0.2682 | H 2 |
| 3 | 0.4544 | 0.1271 | 0.1654 | H 3 |
| 3 | 0.3665 | -0.0664 | 0.1426 | H 4 |
| 3 | 0.1121 | -0.3763 | 0.9043 | H 5 |
| 3 | 0.0449 | -0.5576 | 0.9328 | H 6 |
| 3 | -0.2549 | -0.6349 | 0.8258 | H 7 |
| 3 | -0.2578 | -0.5065 | 0.9066 | H 8 |


| $S$ | 3 | 16 | 10 |
| :--- | :--- | :--- | :--- |


| 3 | 0 | 2.122 | -1.47 |
| :--- | :--- | :--- | :--- |

$\begin{array}{llll}3 & 1 & 1.827 & -0.808\end{array}$
$\begin{array}{llll}3 & 2 & 1.5 & -0.4\end{array}$

| C | 2 | 6 |  |
| :---: | :---: | :---: | :---: |
| 2 | 0 | 1. 625 | -1. 573 |
| 2 | 1 | 1. 625 | -0. 838 |

$\begin{array}{llll}H & 1 & 1 & 0\end{array}$
$101.0 \quad-1.0$
$0 \quad 48 \quad 0 \quad 10$
96.

1. 75
0.01
1

1
$\begin{array}{lllllll}\text { Line } 1 & 5 & 0 & 6 & 0 & 0 & \text { (5I5) }\end{array}$
5: Input file number that is opened as "extdh.dat".
0 : Output of S and H matrices. When 0 or $>90$, the output is suppressed.
6: Output file number that is opened as "extdh.out".
0 : Output of molecular orbital coefficients. When 0 or $>90$, the output is suppressed.
0 : Output of Mulliken charge. When 0 or $>90$, the output is suppressed.
Line $2 \quad 26 \quad 1 \quad$ (2I4)
Number of atoms (If this number is zero, atomic coordinates are read until a blank line appears.)
When 1 the lattice constants are read from the next line. When 0 , the lattice constants are not read, the atomic coordinates are assumed to be given in $\AA \AA$ unit.

| Line 3 | 6.593 | 8.975 | 15.093 | 93.790 | 94.970 | 110.540 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | (6F10.5)

Lattice constants. a, b, c, $\alpha, \beta$, and $\gamma$. When the angles are $90^{\circ}$, the columns may remain blank.
$\begin{array}{llllll}\text { Line } 4 & 1 & 0.4663 & -0.2595 & 0.4475 & (I 4, X, 3 F 10.5) \times 26\end{array}$
Atom species defined by Line 6 and its $\mathrm{x}, \mathrm{y}$, and z coordinates. Atom names are not used inside, but are recommended to be written for your memory.
Line $5 \quad 1$ Blank line
$\begin{array}{lllll}\text { Line } 6 & \mathrm{~S} & 3 & 16 & 10\end{array}$ (A4, 3I4)
Sulfur atom has three kinds of orbitals which are defined by the next lines.
16 and 10 are the numbers of total and core electrons, but these numbers are not used inside the program.
$\begin{array}{llllll}\text { Line } 7 & 3 & 0 & 2.122 & -1.47 & (2 I 4,3 \text { F10.0) } \times 3\end{array}$
3: principal quantum number.
0 : azimuthal quantum number 0 is $\mathrm{s}, 1$ is p and 2 means d orbitals.
2.122 is Slater exponent $\zeta$, and
-1.47 is ionization potential in $\operatorname{Ryd}(-13.6 \mathrm{eV})$.
These values are taken from the previous literatures. ${ }^{3-5} \quad \zeta=0.0$ means double or triple zeta, and requires the next Line $7^{\prime}$.
Line 7'
(I4,X,6F10.5) only when $\zeta=0.0$.
Double $\zeta: \quad 2 \quad \zeta_{1} \quad \mathrm{c}_{1} \quad \zeta_{2} \quad \mathrm{c}_{2}$
$\begin{array}{lllllll}\text { Triple } \zeta: 2 & \zeta_{1} & \mathrm{c}_{1} & \zeta_{2} & \mathrm{c}_{2} & \zeta_{3} & \mathrm{c} 3\end{array}$
Line $8 \quad 1$ Blank line
Repeat Lines 6-8 with the number of atom species.
$\begin{array}{llllll}\text { Line } 9 & 0 & 48 & 0 & 10 & \text { (4I5) }\end{array}$
0 : The number of orbitals, when 0 , the number of total electrons will be given in the next line.
48: Coefficients of the 48th orbital to 48+0th orbital will be written on fort. 10 . For a donor, this number should be the number of HOMO level, then half of the total electrons. For an acceptor this number should be LUMO level, then half of the total electrons and +1 .
When there are more than two independent molecules, change 10 to 20 for the second molecule.
Line $10 \quad 96.0$
The number of total electrons.
$\begin{array}{llll}\text { Line } 11 & 1.75 & 0.01 & 1\end{array}$
(3F10.0)
Coefficient of extended Hückel equation. Usually 1.75.
Line 12 1
(I5)
Number of iterations. Usually 1.
It is, however, not necessary to write down all lines from the first. To make your new extdh.dat from old extdh.dat and at.dat, do the following things.
(1) Open extdh.dat by a text editor.
(2) Delete the old atomic coordinates (Line 4), and copy the atomic coordinates from at.dat generated by trcifg3.exe.
(3) Copy the lattice constants from at.dat.
(4) Change the total number of atoms. (or blank)
(5) Change the total number of electrons.
(6) Save extdh.dat.
(7) Run extdhg3.exe by double clicking the file.
(8) Open extdh.out by a text editor, and check the following points. For BEDT-TTF:

1) The energy level of HOMO (48th level) must be $9.2 \pm 0.1 \mathrm{eV}$.
2) In the list of "CHARGE OF THE 48TH ORBITAL" all the equivalent orbitals have approximately the same charges.
3) In the list of "ATOMIC CHARGE", all atoms of the same kind (for example sulfur) have approximately the same charges. If the atomic coordinates of one atom is incorrect, this number becomes unreasonably large or small.
(9) You can see the molecular orbital coefficients in fort.10, by opening from a text editor. (First start a text editor, and "open" from the editor.)
In case of TTF, all sulfur orbitals have the same sign. The order of the list is $3 \mathrm{~s}, 3 \mathrm{p}_{\mathrm{y}}, 3 \mathrm{p}_{\mathrm{z}}, 3 \mathrm{p}_{\mathrm{x}}, 3 \mathrm{~d}_{\mathrm{xy}}, 3 \mathrm{~d}_{\mathrm{yz}}, 3 \mathrm{~d}_{\mathrm{z}} 2,3 \mathrm{~d}_{\mathrm{xz}}, 3 \mathrm{~d}_{\mathrm{x}} 2-\mathrm{y} 2$ for each sulfur, and $2 \mathrm{~s}, 2 \mathrm{p}_{\mathrm{y}}, 2 \mathrm{p}_{\mathrm{z}}, 2 \mathrm{p}_{\mathrm{x}}$ for each carbon.
4) A. J. Berlinsky, J. F. Carolan, and L Weiler, Solid State Commun., 15, 795 (1974).
5) M.-H. Whangbo a,d R. Hoffmann, J. Am. Chem. Soc., 100, 6093 (1978).
6) J. Am. Chem. Soc., 98, 7252 (1976); 101, 3830 (1979).
(10) (Optional) If the resultsof extdh is no good, it is recommended to try MOPAC. extdhg3.exe generates hdat.dat, which is an input file for MOPAC.
7) From MOPAC, open hdat.dat.
8) [Background][white]
9) Using the rotation bottom, rotate the molecule to display the molecular plane. Hand bottom to fix.
10) $[$ Calculation $][$ Start $]$ to do the single-point calculation (no geometry optimization).
11) [Properties][Molecular orbital] The molecular orbital (HOMO) is displayed.
12) You can display the extdh orbitals by using MOPAC <manual $>$. However, MOPAC does not accept sulfur 3d orbitals. In such a case, delete the S3d orbitals (Line 6 in extdh.dat):

| S | 2 | 16 | 10 |
| :---: | :---: | :---: | :---: |
| 3 | 0 |  | 2.122 |
| 3 | 1 |  | 1.827 |
|  | -1.47 |  |  |
|  |  |  |  |

## 4. Intermolecular Overlap Integrals: SCAL

By using the results of molecular orbital calculation, we can estimate the transfer integrals. Here we assume the transfer integralstare proportional to the intermolecular overlap integrals $S$ as $t=E \times S$, where $E$ is a constant in the order of the energy of the molecular orbital, so we usually use $E=-10 \mathrm{eV}$. Then the estimation of intermolecular overlap integrals is equivalent to the estimation of transfer integrals. We have calculated HOMO of donors, and LUMO of acceptors. The program SCAL reads the coefficient from fort.10. Otherwise, the input data are quite similar to extdh.dat. Before starting the editor, prepare a figure which shows the donor arrangement in the conducting sheet. We usually use a figure that is seen along the molecular long axis. Then specify the original molecule which is given in extdh.dat. This is easily done by obtaining the center of gravity from the midpoint of the central $\mathrm{C}=\mathrm{C}$ bond. Next specify the adjacent molecules which are generated by some kinds of symmetry operations and/or translations. It is frequently necessary to consult International Table for Crystallography to obtained the form of the symmetry operations.
(1) The content of scal.dat is as follows.

| 5 | 6 | 6 | 0 | 0 |
| ---: | ---: | ---: | ---: | ---: |
| 26 | 1 |  | B-(BEDT-TTF) 2IBR2 |  |
| 1 | 0.4663 | -0.2595 | 0.4475 | S 1 |
| 1 | 0.1029 | -0.1444 | 0.4277 | S 2 |
| 1 | 0.2801 | -0.4301 | 0.6217 | S 3 |
| 1 | -0.0817 | -0.3117 | 0.6003 | S 4 |
| 1 | 0.6482 | -0.1383 | 0.2845 | S 5 |
| 1 | 0.2177 | 0.0033 | 0.2619 | S 6 |
| 1 | 0.1959 | -0.5386 | 0.7996 | S 7 |
| 1 | -0.2389 | -0.3973 | 0.7726 | S 8 |
| 2 | 0.2306 | -0.2521 | 0.4874 | C 1 |
| 2 | 0.1531 | -0.3244 | 0.5601 | C 2 |
| 2 | 0.4464 | -0.1575 | 0.3362 | C 3 |
| 2 | 0.2798 | -0.1046 | 0.3451 | C 4 |
| 2 | 0.1154 | -0.4517 | 0.7087 | C |
| 2 | -0.0486 | -0.3972 | 0.6993 | C 6 |
| 2 | 0.6312 | 0.0229 | 0.2263 | C 7 |
| 2 | 0.4268 | 0.0233 | 0.1917 | C 8 |
| 2 | 0.0400 | -0.4922 | 0.8821 | C 9 |
| 2 | -0.1860 | -0.5212 | 0.8527 | C 10 |
| 3 | 0.7181 | 0.0276 | 0.1747 | H 1 |
| 3 | 0.7024 | 0.1220 | 0.2682 | H 2 |
| 3 | 0.4544 | 0.1271 | 0.1654 | H 3 |
| 3 | 0.3665 | -0.0664 | 0.1426 | H 4 |

```
\begin{tabular}{rrrrr}
3 & 0.1121 & -0.3763 & 0.9043 & H5 \\
3 & 0.0449 & -0.5576 & 0.9328 & H6 \\
3 & -0.2549 & -0.6349 & 0.8258 & H7 \\
3 & -0.2578 & -0.5065 & 0.9066 & H8
\end{tabular}
S 3 16 10
3
3 1 1.827 -0.808
3 2 1.5 -0.4
C 2 6 2
2
2 1 1.625 -0.838
H 1 1 0
10}1.0-1.
\begin{tabular}{|c|c|c|c|c|c|}
\hline 1. 75 & 0.01 & 1 & & & \\
\hline 6. 593 & 8. 975 & 15. 093 & 93.79 & 94.97 & 110. 54 \\
\hline 1.00 .0 & 0.000 & 1.00 .0 & \(0.0 \quad 0.0\) & \(1.0 \quad 0.0\) & \(0.0 \quad 0.0\) \\
\hline -1.0 0.0 & \(0.0 \quad 0.0\) & -1.0 0.0 & \(0.0 \quad 0.0\) & -1.0 0.0 & \(0.0 \quad 1.0\) \\
\hline
\end{tabular}
10.0
    120 1 10
0.0 0.0 0.0
1.0}00.0\quad0.
0.0 -1.0 0.0
1.0 1.0 0.0
10.0
1 2
2 1 1
2 1
2 2
3 1 2
4 1
Line \(1 \quad 5 \quad 0 \quad 6\)
5: Input file number that is opened as "scal.dat".
0 : Output of coefficients and rectangular coordinates.
6: Output file number that is opened as "sdat.d1".
Line 2 26 1
Number of atoms. The next 1 is not used in the program.
\(\begin{array}{llllll}\text { Line } 3 & 1 & 0.4663 & -0.2595 & 0.4475 & (I 4, X, 3 F 10.5) \times 26\end{array}\)
```

Atom species defined by Line 5 and its $\mathrm{x}, \mathrm{y}$, and z coordinates. Atom names are not used inside, but are recommended to be written for your memory.
Line $4 \quad 1$ Blank line
$\begin{array}{llllll}\text { Line } 5 & \mathrm{~S} & 3 & 16 & 10 & (\mathrm{~A} 4,3 \mathrm{I} 4)\end{array}$
Sulfur atom has three kinds of orbitals which are defined by the next lines.
16 and 10 are the numbers of total and core electrons, but these numbers are not used inside the program.
$\begin{array}{llllll}\text { Line } 6 & 3 & 0 & 2.122 & -1.47 & (2 I 4,3 F 10.0) \times 3\end{array}$
3: principal quantum number.
0 : azimuthal quantum number 0 is $\mathrm{s}, 1$ is p and 2 means d orbitals.
2.122 is Slater exponent $\zeta$, and
-1.47 is ionization potential in Ryd ( -13.6 eV ).
These values are taken from the previous literatures. ${ }^{3-5} \quad \zeta=0.0$ means double or triple zeta, and requires the next line.
Line 6'
$\begin{array}{llllll}\text { Double } \zeta: & 2 & \zeta_{1} & \mathrm{c}_{1} & \zeta_{2} & \mathrm{c}_{2}\end{array}$
$\begin{array}{lllllll}\text { Triple } \zeta: 2 & \zeta_{1} & \mathrm{c} 1 & \zeta_{2} & \mathrm{c} 2 & \zeta_{3} & \mathrm{c} 3\end{array}$

## Line $7 \quad 1$ Blank line

Repeat Lines 5-7 with the number of atom species.
Line $81.750 .01 \quad 1 \quad$ (3F10.0)
Coefficient of extended Hückel equation. Usually 1.75 .
$\begin{array}{lllllll}\text { Line } 9 & 6.593 & 8.975 & 15.093 & 93.790 & 94.970 & 110.540\end{array}$ (6F10.5)
Lattice constants. $\mathrm{a}, \mathrm{b}, \mathrm{c}, \alpha, \beta$, and $\gamma$. When the angles are $90^{\circ}$, the columns may remain blank.
$\begin{array}{llllllllllll}\text { Line } 10 & 1.0 & 0.0 & 0.0 & 0.0 & 1.0 & 0.0 & 0.0 & 0.0 & 1.0 & 0.0 & 0.0\end{array} \quad 0.0$
(12F5.0) xNUNIT
Symmetry operations
(x') (CK(1)CK(2)
CK(3))(x) (CK(10))
$\left(y^{\prime}\right)=(\mathrm{CK}(4) \mathrm{CK}(5) \quad \mathrm{CK}(6))(\mathrm{y}) \quad+(\mathrm{CK}(11))$
(z') (CK(7)CK(8) CK(9))(z) (CK(12))
When $\mathrm{CK}(1) \geq 10.0$, proceed to the next line.
$\begin{array}{lllll}\text { Line } 11 & 120 \quad 1 & 10 & \text { (5I5) }\end{array}$
120: The number of orbitals on a molecule. This number should be the same as that calculated in EXTDH (1).
1: Coefficients of one molecule is read from fort.10. If there are two independent molecule, change this line to
$120 \quad 2 \quad 10 \quad 20$.
After the NCELL molecules are read from fort.10, fort. 20 ,etc, these molecules are duplicated by the symmetry operations given in Line 10 . If NUNIT symmetry operations are read from Line 10 , the total number of molecules are NCELL x NUNIT. Then the unit cell contains NCELL x NUNIT molecules.
$\begin{array}{lllll}\text { Line } 12 & 0.0 & 0.0 & 0.0 & \text { (3F5.0) }\end{array}$
Translation that is applied to the molecules in Line 11. When $x \geq 10.0$, proceed to the next line.
Line 133013

Calculate the overlap integral between the first molecule in the original cell and the second molecule in the cell generated by the third translation (Line 12). End of calculation if the first number is zero.
(2) To understand the above example, see Figure 1. The center of the donor molecule whose coordinates are given is at $(0.25,-0.27$, 0.50 ); this is the center of C 1 and C 2 . This molecule is designated as A in Figure 1 (add +b ). By a symmetry operation ( $-x,-y, 1-z$ ) (Line 10), the molecule moves to E. The first overlap, 112 (Line 13) specifies this overlap, giving q1. The second translation (1.0, 0.0, 0.0) (Line 12) generates I and C. Thus, the following overlaps are estimated:

| $(0.0,0.0,0.0) 2$ | 1 | 1 | A-E | q1 |
| :--- | :--- | :--- | :--- | :--- |
| $(1.0,0.0,0.0) 2$ | 1 | 1 | A-I | c |
| $(1.0,0.0,0.0) 2$ | 1 | 2 | A-C | p2 |
| $(0.0,-1.0,0.0) 3$ | 1 | 2 | A-B | p1 |
| $(1.0,-1.0,0.0) 4$ | 1 | 2 | A-H | q2 |



Figure 1 Molecular packing of $\beta$-(BEDT-TTF) $)_{3} I_{3}$.

It is not necessary to write down all lines from the first. If scal.dat is made from old scal.dat and extdh.dat, do the following things.

1) Move the atomic coordinates to the proper position, and delete the old ones.
2) Move the lattice constants to the proper position.
3) Edit Lines $10-13$ by following the above instructions.

Finally run scal by double clicking the file.

## 5. Tight-Binding Energy Band Calculation: TBMAP

By using the overlap integrals calculated by SCAL, the energy band and the Fermi surface are calculated.
(1) The content of tbmap.dat is as follows.
6. 593
8. 975
15. 093
93. 79
94.97
110. 54
$20.0 \quad 0.0$
$-0.0225-0.0111 \quad-0.0125 \quad-0.00711-0.0061$
$\begin{array}{lll}0.0 & 0.0 & 0.0\end{array}$
0330
$\begin{array}{lll}1.0 & 0.0 & 0.0\end{array}$
5205
$0.0 \quad 1.0 \quad 0.0$
0010
$1.0 \quad-1.0 \quad 0.0$
0400
10.0
$\begin{array}{rrrccc}2 & 1 & 3 & 20 & -25 & 3 \\ 0.02 & & -0.7 & 0.7 & & 0.75\end{array}$
1
$\begin{array}{llll}0 & 100.0 & 0.0 & 0.0\end{array}$
$0101.0-1.00 .0$
$\begin{array}{lllllllll}1 & 101.0 & -1.0 & 0.0 & 1.0 & 0.0 & 0.0 & 3 & 0.0\end{array}$
$\begin{array}{llll}0 & 101.0 & 0.0 & 0.0\end{array}$
$0100.0 \quad 0.0 \quad 0.0$
$\begin{array}{llll}0 & 100.0 & 1.0 & 0.0\end{array}$
$\begin{array}{lllllllll}1 & 100.0 & 1.0 & 0.0 & 1.0 & 0.0 & 0.0 & 3 & 0.0\end{array}$
10
11
Line $16.593 \quad 8.975 \quad 15.093 \quad 93.79 \quad 94.97 \quad 110.54$ (6F10.0)
Lattice constants. a, b, c, $\alpha, \beta$, and $\gamma$. When the angles are $90^{\circ}$, the columns may remain blank.
Line 2 2
(I5, 12F5.0)
A unit cell contains two molecules. If the energy levels of these molecules are different owing to charge separation, write the difference.
Line 300 (12F5.0)
Positions of molecules. All molecules may be put on ( $0.0,0.0,0.0$ ).
Line $4-0.0225-0.0111 \quad-0.0125 \quad-0.00711-0.0061 \quad$ (6F10.0)
p1 p2 q1 q2 c

Overlap integrals calculated by SCAL. When zero appears at the $n$-th entry, the number of the overlap is assumed to be $n-1$. The maximum number of these lines is two, so that we can put maximum 12 overlaps. When the number of the overlaps are just six, input the second blank line. If $n$ is less than six, the second line is not necessary.
Line 5 Blank
The value of $E$ in $t=E \times S$. If this line is blank, $E=-10 \mathrm{eV}$ is assumed.
$\begin{array}{llll}\text { Line } 6 & 0.0 & 0.0 & 0.0\end{array}$
(3F10.0)
Translation that specifies the neighboring cell.
$\begin{array}{lllll}\text { Line } 7 & 0 & 3 & 3 & 0\end{array}$
This means a matrix like:
$0 \quad 3$
30
3 means the first overlap read in Line 4 is placed between the first molecule in the original cell and the second molecule in the translated cell. Now the translation is $(0.0,0.0,0.0)$ so that this matrix represents the overlaps within the original cell. The first translation should be always ( $0.0,0.0,0.0$ ), in which the diagonal elements are zero and the non-diagonal elements are symmetrical.
Lines 6 and 7 are repeated until all interactions are covered. When $x \geq 10.0$ appears, proceed to the next input.

The above example is for $\beta$-(BEDT-TTF)2I3 shown in Figure 1. Two molecules in the original unit cell are designated as A and E in Figure 1. As for the original cell $(0.0,0.0,0.0)$, the matrix is

03
30
so that between $A$ and $E$ is the first overlap. The numbering of the overlap follows the order of Line 4 , then the first overlap is $q 1$. The second translation $(1.0,0.0,0.0)$ is accompanied by the matrix
$\begin{array}{ll}5 & 2 \\ 0 & 5 .\end{array}$
From the first molecule (A) in the original cell to the second molecule (I) in the translated cell, there is the fifth overlap (c). The next translation is $(0.0,1.0,0.0)$ with the matrix

| 0 | 0 |
| :--- | :--- |
| 1 | 0. |

This translation generates F , so that form E to F is the first overlap ( p 1 ). The final translation (1.0, $-1.0,0.0$ ) covers the A-H interaction designated as q 2 .
$0 \quad 4$
$0 \quad 0$

## $\begin{array}{lllllllll}\text { Line } 8 & 2 & 1 & 3 & 20 & -25 & 1 & 0.0 & (615, ~ F 10.0)\end{array}$

2: Horizontal axis of the map and the drawing of the Fermi surface is $k_{\mathrm{b}}$-axis.
1: Vertical axis of the map and the drawing of the Fermi surface is $k_{\mathrm{a}}$-axis.
3: Section of the map is $k_{\mathrm{c}}$-axis.
20: The mesh of the horizontal axis is 20 . Then the map is calculated from $k_{\mathrm{b}}=$ 0.0 to $k_{\mathrm{b}}=\pi / b$ with the interval of $\pi / 20 b$.
-25 : The mesh of the vertical axis is 25 . Then the map is calculated from $k_{\mathrm{a}}=$ $-\pi / b \quad$ to $k_{\mathrm{a}}=\pi / b$ with the interval of $\pi / 25 a$.
1: The mesh of the $k_{\mathrm{c}}$-axis is one, Then the map is calculated only at $k_{\mathrm{c}}=0.0$.
The map is written in meV unit. If you want to change this scale, the output energy is multiplied by this number. 1000 is the default.
Line $90.02 \quad-0.5 \quad 0.5 \quad 0.75$
(4F10.0)
Calculation of the density of states. The program counts the number of states starting from -0.5 eV to 0.5 eV with the interval of 0.02 eV . Fill 0.75 of this band. 1.0 corresponds to totally filled, 0.75 to quarter filled ( $2: 1$ composition), and 0.5 to half-filled. The Fermi surface is searched on the basis of this number.
Line $10 \quad 1$
Draw the energy band diagram, when 1. Not draw when 0 .
$\begin{array}{cccccc}\text { Line } 11 & 0 & 10 & 0.0 & 0.0 & 0.0 \\ 0 & 5 & 1.0 & -1.0 & 0.0\end{array}$
(2I5, 3F10.0)
Instruction for drawing the energy band diagram. The program calculates the energy band from the $\Gamma$ point $(0.0,0.0,0.0)$ to $(\pi / a,-\pi / b, 0.0)$ with $1 / 10$ intervals. The above input generates the following sequence as shown in Figure 2. If the first number is not zero like,

$$
\begin{array}{llllllllll}
1 & 5 & 1.0 & -1.0 & 0.0 & 1.0 & 0.0 & 0.0 & 3 & 0.0
\end{array}
$$

this means the crossing point of the lines going through $(\pi / a,-\pi / b, 0.0)$ and $(\pi / a$, $0.0,0.0$ ), then the V point in Figure 2. The final "3 0.0 " stands for $k_{\mathrm{Z}}=0.0$ at this crossing point. When the first column is greater than 2 , proceed to the next line.
Line 12
11
(2I1)
Draw the Fermi surface diagram, when 1. Not draw when 0.
After the above input sequence is completed, run tbmap.exe by double clicking the file. The output file is "tbmap.out". then open the file and check the calculation is correctly finished. In particular check the histogram of the density of states, and the range of energy is larger than the range of actual energy bands. If the histogram overflows the range, change the limits of Line 8.

The drawing is plotted by double clicking fermi.plt. Alternatively, you can open fermi.plt of your folder from gnuplot.

The output file is stored in "tbmap.ps", double clicking it makes tbmap.pdf.

## 5. Geometry of Molecules: PLANEA

To analyze the geometry of two molecules that give the above overlap integrals, define the "molecular coordinates" and calculate the " $x, y, z$, and $\varphi$ ".
(1) The content of planea.dat is as follows:


Line $1 \quad 5 \quad 996$
5: Input file number that is opened as "planea.dat".

99: Not used.
6: Output file number that is opened as "padat.d1".
Line 2141
(2I4)
Number of atoms. Only input the atoms that define the molecular plane following Figure, so this number is 6,10 or 14 . 1 is not used.
Line $3 \quad 10.082 \quad 20.565 \quad 9.933 \quad 103.700 \quad 90.91 \quad 93.060$ (6F10.5)
Lattice constants. $\mathrm{a}, \mathrm{b}, \mathrm{c}, \alpha, \beta$, and $\gamma$. When the angles are $90^{\circ}$, the columns may remain blank.
$\begin{array}{llll}\text { Line } 42 & 0.9730 & 0.4678 & 0.4860\end{array}$
(I4,X,3F10.0)
Atomic coordinates. The atoms must be arranged in the order of Figure.

## Line 5

5
(I5)
The number of symmetry operations read in the next lines 6 .
Line 61.00 .00 .00 .01 .00 .00 .00 .01 .00 .01 .00 .0
Symmetry operations
$\begin{array}{llll}\left(\mathrm{x}^{\prime}\right) & (\mathrm{CK}(1) \mathrm{CK}(2) & \mathrm{CK}(3))(\mathrm{x}) & (\mathrm{CK}(10)) \\ \left(\mathrm{y}^{\prime}\right)= & \text { (CK(4)CK(5) } & \mathrm{CK}(6))(\mathrm{y}) & +\quad(\mathrm{CK}(11))\end{array}$
(z') (CK(7)CK(8) CK(9))(z) (CK(12))
The computer calculates the molecular coordinates of the original molecule, and after this symmetry operation, the position of the moved molecule is calculated and represented by the "molecular coordinates".
If there are more than two crystallographically independent molecules, we have to input the second molecule. In that case input $\mathrm{CK}(1) \geq 20.0$, and new atomic coordinates are read after the input of Line 6 . After once $\mathrm{CK}(1) \geq 20.0$ appears, the coordinates of the moved molecule are generated from the new coordinates. In this way we can estimate all A-A and A-B geometries, but we cannot obtain the geometries of B-B interactions. To calculate these interactions, input the coordinates of the B molecule from the first, and run the program again.

Lines 1 to 3 are the same as extdh.dat. Rearrange the order of the atoms, and after those, newly write Lines 5 and 6.

After saving the results to planea.dat, run the program by double clicking the exe file.

