

Energy Band Calculation of Molecular Conductors

(For windows)

Revised April 2024

Examples of scal.dat and tmap.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
tmap.exe tmap.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 1 1 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

1 1.0 0.0 1.0 (I5, 3F5.0)

(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 3s, three 3p (namely $3p_x$, $3p_y$, and $3p_z$), and five 3d orbitals, then there are $1 + 3 + 5 = 9$ orbitals on each S atom. A carbon has $2s + 2p = 4$ orbitals, and a hydrogen has one 1s orbital. Therefore, the total number of orbitals are 120. We will use these numbers later.

(2) The content of extdh.dat is as follows.

```

5 0 6 0 0 B-(BEDT-TTF)2IBR2
26 1
6.593 8.975 15.093 93.790 94.970 110.540
1 0.4663 -0.2595 0.4475 S1
1 0.1029 -0.1444 0.4277 S2
1 0.2801 -0.4301 0.6217 S3
1 -0.0817 -0.3117 0.6003 S4
1 0.6482 -0.1383 0.2845 S5
1 0.2177 0.0033 0.2619 S6
1 0.1959 -0.5386 0.7996 S7
1 -0.2389 -0.3973 0.7726 S8
2 0.2306 -0.2521 0.4874 C1
2 0.1531 -0.3244 0.5601 C2
2 0.4464 -0.1575 0.3362 C3
2 0.2798 -0.1046 0.3451 C4
2 0.1154 -0.4517 0.7087 C5

```

2	-0.0486	-0.3972	0.6993	C6
2	0.6312	0.0229	0.2263	C7
2	0.4268	0.0233	0.1917	C8
2	0.0400	-0.4922	0.8821	C9
2	-0.1860	-0.5212	0.8527	C10
3	0.7181	0.0276	0.1747	H1
3	0.7024	0.1220	0.2682	H2
3	0.4544	0.1271	0.1654	H3
3	0.3665	-0.0664	0.1426	H4
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

S	3	16	10	
3	0	2.122	-1.47	
3	1	1.827	-0.808	
3	2	1.5	-0.4	

C	2	6	2	
2	0	1.625	-1.573	
2	1	1.625	-0.838	

H	1	1	0	
1	0	1.0	-1.0	

0	48	0	10	
96.	1.75	0.01	1	
1				

Line 1 5 0 6 0 0 (5I5)

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 26 1 (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 Å unit.

- (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 ± 0.1 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 3s, 3py, 3pz, 3px, 3dxy, 3dyz, 3dz2, 3dxz, 3dx2-y2 for each sulfur, and 2s, 2py, 2pz, 2px for each carbon.

- 3) A. J. Berlinsky, J. F. Carolan, and L Weiler, *Solid State Commun.*, **15**, 795 (1974).
- 4) M.-H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 6093 (1978).
- 5) *J. Am. Chem. Soc.*, **98**, 7252 (1976); 101, 3830 (1979).

(10) (Optional) If the results of extdh is no good, it is recommended to try [MOPAC](#). extdhg3.exe generates hdat.dat, which is an input file for MOPAC.

- 1) From MOPAC, open hdat.dat.
- 2) [Background][white]
- 3) Using the rotation bottom, rotate the molecule to display the molecular plane. Hand bottom to fix.
- 4) [Calculation][Start] to do the single-point calculation (no geometry optimization).
- 5) [Properties][Molecular orbital] The molecular orbital (HOMO) is displayed.

6) 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  -1.47
3   1     1.827  -0.808

```

4. Intermolecular Overlap Integrals: SCAL

By using the results of molecular orbital calculation, we can estimate the transfer integrals. Here we assume the transfer integrals are 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 $E = -10$ 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 C=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 obtain the form of the symmetry operations.

(1) The content of scal.dat is as follows.

```
5 6 6 0 0 B-(BEDT-TTF)2IBR2
26 1
1 0.4663 -0.2595 0.4475 S1
1 0.1029 -0.1444 0.4277 S2
1 0.2801 -0.4301 0.6217 S3
1 -0.0817 -0.3117 0.6003 S4
1 0.6482 -0.1383 0.2845 S5
1 0.2177 0.0033 0.2619 S6
1 0.1959 -0.5386 0.7996 S7
1 -0.2389 -0.3973 0.7726 S8
2 0.2306 -0.2521 0.4874 C1
2 0.1531 -0.3244 0.5601 C2
2 0.4464 -0.1575 0.3362 C3
2 0.2798 -0.1046 0.3451 C4
2 0.1154 -0.4517 0.7087 C5
2 -0.0486 -0.3972 0.6993 C6
2 0.6312 0.0229 0.2263 C7
2 0.4268 0.0233 0.1917 C8
2 0.0400 -0.4922 0.8821 C9
2 -0.1860 -0.5212 0.8527 C10
3 0.7181 0.0276 0.1747 H1
3 0.7024 0.1220 0.2682 H2
3 0.4544 0.1271 0.1654 H3
3 0.3665 -0.0664 0.1426 H4
```

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

S	3	16	10	
3	0	2.122	-1.47	
3	1	1.827	-0.808	
3	2	1.5	-0.4	

C	2	6	2	
2	0	1.625	-1.573	
2	1	1.625	-0.838	

H	1	1	0	
1	0	1.0	-1.0	

1.75	0.01	1			
6.593	8.975	15.093	93.79	94.97	110.54
1.0	0.0	0.0	0.0	1.0	0.0
-1.0	0.0	0.0	0.0	-1.0	0.0

10.0					
120	1	10			
0.0	0.0	0.0			
1.0	0.0	0.0			
0.0	-1.0	0.0			
1.0	1.0	0.0			
10.0					

1	1	2
2	1	1
2	2	1
2	2	2
3	1	2
4	2	1

Line 1 5 0 6 (3I5)

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 (2I4)

Number of atoms. The next 1 is not used in the program.

Line 3 1 0.4663 -0.2595 0.4475 (I4,X,3F10.5) x26

Atom species defined by Line 5 and its x, y, and z coordinates. Atom names are not used inside, but are recommended to be written for your memory.

Line 4 1 Blank line

Line 5 S 3 16 10 (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.

Line 6 3 0 2.122 -1.47 (2I4, 3F10.0) x3

3: principal quantum number.

0: azimuthal quantum number 0 is s, 1 is p and 2 means d orbitals.

2.122 is Slater exponent ζ , and

-1.47 is ionization potential in Ryd (-13.6 eV).

These values are taken from the previous literatures.³⁻⁵ $\zeta=0.0$ means double or triple zeta, and requires the next line.

Line 6' (I4,X,6F10.5) only when $\zeta=0.0$.

Double ζ : 2 ζ_1 c1 ζ_2 c2

Triple ζ : 2 ζ_1 c1 ζ_2 c2 ζ_3 c3

Line 7 1 Blank line

Repeat Lines 5 - 7 with the number of atom species.

Line 8 1.75 0.01 1 (3F10.0)

Coefficient of extended Hückel equation. Usually 1.75.

Line 9 6.593 8.975 15.093 93.790 94.970 110.540
(6F10.5)

Lattice constants. a, b, c, α , β , and γ . When the angles are 90°, the columns may remain blank.

Line 10 1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0
(12F5.0) xNUNIT

Symmetry operations

(x') (CK(1)CK(2) CK(3))(x) (CK(10))

(y') = (CK(4)CK(5) CK(6))(y) +(CK(11))

(z') (CK(7)CK(8) CK(9))(z) (CK(12))

When CK(1) \geq 10.0, proceed to the next line.

Line 11 120 1 10 (5I5)

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 2 10 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.

Line 12 0.0 0.0 0.0 (3F5.0)

Translation that is applied to the molecules in Line 11.

When x \geq 10.0, proceed to the next line.

Line 13 3 1 2 (3I5)

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 C1 and C2. 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, 1 1 2 (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

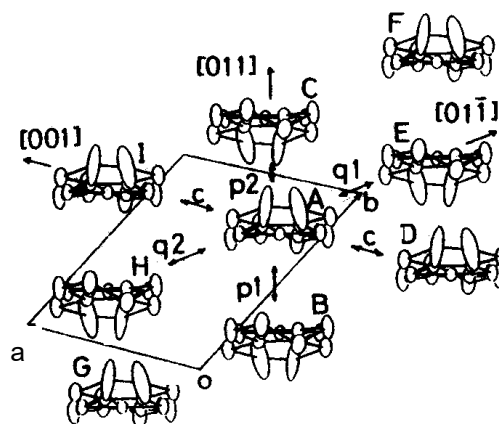


Figure 1 Molecular packing of β -(BEDT-TTF) $_2$ I $_3$.

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 tmap.dat is as follows.

```
6.593    8.975    15.093    93.79    94.97    110.54
    20.0    0.0
```

```
-0.0225  -0.0111  -0.0125  -0.00711  -0.0061
```

```
0.0      0.0      0.0
```

```
0 3 3 0
```

```
1.0      0.0      0.0
```

```
5 2 0 5
```

```
0.0      1.0      0.0
```

```
0 0 1 0
```

```
1.0      -1.0     0.0
```

```
0 4 0 0
```

```
10.0
```

```
    2    1    3    20  -25    3
```

```
0.02    -0.7    0.7    0.75
```

```
1
```

```
0 100.0  0.0  0.0
```

```
0 101.0 -1.0  0.0
```

```
1 101.0 -1.0  0.0  1.0  0.0  0.0    3  0.0
```

```
0 101.0  0.0  0.0
```

```
0 100.0  0.0  0.0
```

```
0 100.0  1.0  0.0
```

```
1 100.0  1.0  0.0  1.0  0.0  0.0    3  0.0
```

```
10
```

```
11
```

Line 1 6.593 8.975 15.093 93.79 94.97 110.54 (6F10.0)

Lattice constants. a, b, c, α , β , and γ . When the angles are 90° , the columns may remain blank.

Line 2 2 (15, 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 3 0 (12F5.0)

Positions of molecules. All molecules may be put on (0.0, 0.0, 0.0).

Line 4 -0.0225 -0.0111 -0.0125 -0.00711 -0.0061 (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 (F10.0)

The value of E in $t = E \times S$. If this line is blank, $E = -10$ eV is assumed.

Line 6 0.0 0.0 0.0 (3F10.0)

Translation that specifies the neighboring cell.

Line 7 0 3 3 0 (30I2)

This means a matrix like:

$$\begin{matrix} 0 & 3 \\ 3 & 0 \end{matrix}$$

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 β -(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

$$\begin{matrix} 0 & 3 \\ 3 & 0 \end{matrix}$$

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 q1. The second translation (1.0, 0.0, 0.0) is accompanied by the matrix

$$\begin{matrix} 5 & 2 \\ 0 & 5. \end{matrix}$$

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

$$\begin{matrix} 0 & 0 \\ 1 & 0. \end{matrix}$$

This translation generates F, so that from E to F is the first overlap (p1). The final translation (1.0, -1.0, 0.0) covers the A-H interaction designated as q2.

$$\begin{matrix} 0 & 4 \end{matrix}$$

$$\begin{matrix} 0 & 0 \end{matrix}$$
