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 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 treifg3.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	Elec	trons	Orbi	tals
	S	8	6	48	9	72
	С	10	4	40	4	40
	Η	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 26	0 1	6	0	0 B-	(BEDT	TTF)21BR	2			
20	6. 593	3	8.	975	15.	093	93.	790	94.	970	110. 540
1	(0. 46	63	-0.2	595	0.4	1475		S1		
1	(0. 10	29	-0.1	444	0.4	1277		S2		
1	(0. 28	01	-0.4	301	0.6	6217		S3		
1	-(0. 08	17	-0.3	117	0.6	6003		S4		
1	(0. 64	82	-0.1	383	0.2	2845		S5		
1	(). 21 [°]	77	0.0	033	0.2	2619		S6		
1	(0. 19	59	-0.5	386	0.7	7996		S7		
1	-(0. 23	89	-0.3	973	0.7	7726		S8		
2	(0. 23	06	-0.2	521	0.4	1874		C1		
2	(0. 15	31	-0.3	244	0.5	5601		C2		
2	(0.44	64	-0.1	575	0.3	3362		C3		
2	(). 27	98	-0.1	046	0.3	3451		C4		
2	(0. 11	54	-0.4	517	0.7	7087		C5		

2	-0. 0486	-0. 3972	0. 6993	
2	0. 6312	0. 0229	0. 2263	
2	0. 4268	0. 0233	0. 1917	
2	0.0400	-0. 4922	0. 8821	
2	-0. 1860	-0. 5212	0. 8527	
3	0. 7181	0. 0276	0. 1747	
3	0. 7024	0. 1220	0. 2682	
3	0. 4544	0. 1271	0. 1654	
3	0. 3665	-0.0664	0. 1426	
3	0. 1121	-0. 3763	0. 9043	
3	0. 0449	-0. 5576	0. 9328	
3	-0. 2549	-0. 6349	0. 8258	
3	-0. 2578	-0. 5065	0. 9066	
S	3 16 10			
3	0 2.1	22 –1.47		
3	1 1.8	27 –0. 808		
3	2 1.5	-0.4		
С	2 6 2			
2	0 1.625	-1.573		
2	1 1.625	-0.838		
Н	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 (2I4) 1 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.

C6 C7 C8 C9 C10 H1 H2 H3 H4 H5 H6 H7 H8

Line	3 6.593 (6F10.5)	8.975	15.09	93	93.79()	94.970	110.540
	Lattice constant remain blank.	ts. a, b, c	α, β, α	nd γ.	When	the ar	igles are	e 90°, the columns may
Line	4 1	0.4663	-0.25	95	0.447	5		(I4,X,3F10.5) ×26
	Atom species d	efined by	Line 6	and its	s x, y, a	and z o	coordina	ates. Atom names are
	not used inside,	but are i	recomme	nded t	o be w	ritten	for you	memory.
Line	5 1 Blan	k line						
Line	6 S	3	16 1	0			(A4, 1	3I4)
	Sulfur atom has	three kin	nds of or	bitals	which a	are de	fined by	the next lines.
	16 and 10 are t	he numb	ers of to	tal and	d core	electro	ons, but	these numbers are not
	used inside the	program.						
Line	7 3	0	2.122		-1.47		(2I4,	3F10.0) ×3
	3: principal qua	intum nu	mber.					
	0: azimuthal qu	antum n	umber 0	is s, 1	is p an	d 2 me	eans d o	rbitals.
	2.122 is Slater e	exponent	ζ , and					
	-1.47 is ionizati	on poten	tial in R	yd (-13	3.6 eV)	•		
	These values an	e taken :	from the	previo	ous lite	rature	s.3-5	ζ=0.0 means double or
	triple zeta, and	requires	the next	Line 7	".			
Line	7'				(I4,X,6	F10.5) only v	vhen ζ=0.0.
	Double ζ:	2	ζ ₁ c	1	ζ2	c2		
	Triple ζ: 2	ζ1	c1 C	2	c2	ζ3	c3	
Line	8 1 Blan	k line		-	-	50	C	
Line	Repeat Lines 6	- 8 with	the numł	er of a	atom sr	necies		
Line	9 0	48	0 1	0		(4I5)		
	0: The number	of orbita	ls, when	0, the	e numb	er of t	total ele	ctrons will be given in
	the next line.							C
	48: Coefficient	s of the	48th orb	oital to	48+0t	h orbi	ital will	be written on fort.10.
	For a donor, the	is numbe	er should	l be the	e numł	ber of	НОМО	level, then half of the
	total electrons.	For an	acceptor	this n	umber	shoul	d be LU	MO level, then half of
	the total electro	ns and +	1.					
	When there are	e more tl	nan two	indepe	endent	molec	cules, cl	nange 10 to 20 for the
	second molecul	e.						
Line	10 96.0					(F4.0)	
	The number of	total elec	trons.					
Line	11 1.75	0.01	1			(3F10	0.0)	
	Coefficient of e	xtended	Hückel e	equatio	on. Us	sually	1.75.	
Line	12 1					(I5)		
	Number of itera	tions.	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 ± 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, $3p_y$, $3p_z$, $3p_x$, $3d_{xy}$, $3d_{yz}$, $3d_z^2$, $3d_{xz}$, $3d_x^2-y^2$ for each sulfur, and

2s, $2p_V$, $2p_Z$, $2p_X$ for each carbon.

3) A. J. Berlinsky, J. F. Carolan, and L Weiler, Solid State Commun., 15, 795 (1974).

4) M.-H. Whangbo a,d 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 \underline{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 <<u>manual</u>>. 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 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 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 obtained the form of the symmetry operations.

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

5	6	6	0	0 B-	(BEDT-TTF) 21BR2	
26	1					
1	0.4	663	-0.	2595	0.4475	S1
1	0.1	029	-0.	1444	0. 4277	S2
1	0.2	801	-0.	4301	0.6217	S3
1	-0.0	817	-0.	3117	0.6003	S4
1	0.6	482	-0.	1383	0. 2845	S5
1	0.2	177	0.	0033	0.2619	S6
1	0.1	959	-0.	5386	0.7996	S7
1	-0.2	389	-0.	3973	0. 7726	S8
2	0.2	306	-0.	2521	0. 4874	C1
2	0.1	531	-0.	3244	0.5601	C2
2	0.4	464	-0.	1575	0.3362	C3
2	0.2	798	-0.	1046	0. 3451	C4
2	0.1	154	-0.	4517	0. 7087	C5
2	-0.0	486	-0.	3972	0. 6993	C6
2	0.6	312	0.	0229	0. 2263	C7
2	0.4	268	0.	0233	0. 1917	C8
2	0.0	400	-0.	4922	0. 8821	C9
2	-0.1	860	-0.	5212	0.8527	C10
3	0.7	181	0.	0276	0. 1747	H1
3	0.7	024	0.	1220	0.2682	H2
3	0.4	544	0.	1271	0. 1654	H3
3	0.3	665	-0.	0664	0. 1426	H4

-0.3763 0.9043 H5 3 0.1121 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 2.122 -1.47 0 3 1.827 -0.808 1 3 2 1.5 -0.4 С 2 6 2 2 0 1.625 -1.573 2 1.625 -0.838 1 Η 1 1 0 0 1.0 1 -1.0 1.75 0.01 1 6.593 15.093 93.79 8.975 94.97 110.54 1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 -1.00.00.000.0 $-1.\ 0\ 0.\ 0\ 0.\ 0\ 0.\ 0\ -1.\ 0\ 0.\ 0\ 0\ 1.\ 0$ 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

		tes defined t	by Line	J and I	ts л, у	, and Z	coorun	lates.	Atom names are
	not used in	side, but are	recom	mended	to be	written	for you	ır memor	ry.
Line	4 1	Blank line							
Line	5 S	3	16	10			(A4,	, 3I4)	
	Sulfur atom	n has three k	inds of	orbitals	s whicl	h are de	efined b	y the nex	xt lines.
	16 and 10	are the num	bers of	total a	nd core	e electr	ons, bu	t these n	umbers are not
	used inside	the program	1.						
Line	6 3	0	2.122		-1.47		(214	, 3F10.0)) x3
	3: principal	l quantum n	umber.						
	0: azimutha	al quantum 1	number	0 is s, 1	l is p a	nd 2 m	ieans d	orbitals.	
	2.122 is Sla	ater exponer	nt ζ, and	d	-				
	-1.47 is ion	nization pote	ntial in	Ryd (-	13.6 eV	V).			
	These valu	es are taken	from t	he prev	ious li	terature	es.3-5	ζ=0.0 m	neans double or
	triple zeta.	and requires	s the ne	xt line.					
Line	6'				(I4.X	.6F10.	5) only	when $\zeta=$	0.0.
	Double Z:	2	۲۱	c1	رى	c7	, ,	C	
	Triple $\zeta \cdot 2$	٢1	c1	5	c2	<u>م</u>	c2		
т :	$\frac{1}{7}$	Rlank line	•1	54	U_	53	•3		
Line	Donast Lin	og 5 7 with	tha nu	mborot	Fatom	smaaia			
I inc	Repeat Lin	01 1	i ine nu	mber of	(2E1)	species	5.		
Line	6 1.73 0.	01 1	l Uüalıa	1 aquat	(3F1)	0.0) Ugualla	1 75		
I inc	6502		і писке 15		$\begin{array}{c} 1011. \\ 02.7 \end{array}$	Osually	(1./J. 04.070	1104	540
Line	9 0.393 (6F10.5)	8.973	13	.095	93.7	90	94.970	110	040
	Lattice con	stants a h	c a B	andy	XX 71	n tha a	nalaa a	re 90° th	e columns may
	Lattice con	istants. a. D.	U. U. D .	anu y.	wne	n the a	ligies al	v .v . u	
	remain bla	nk.	ι , α, ρ,	, anu <i>γ</i> .	wne	n the a	ligies a	ie 90 , iii	e corumns may
Line	remain blan 10 1.0 0.0	nk. 0.0 0.0	1.0 0	.0 0.0	0.0	1.0 0	.0 0.0	0.0	e corunnis may
Line	remain blan 10 1.0 0.0	nk. 0.0 0.0	1.0 0	.0 0.0	0.0	1.0 0	.0 0.0	0.0 (12F5	5.0) xNUNIT
Line	remain blan 10 1.0 0.0 Symmetry	nk. 0.0 0.0 operations	1.0 0	.0 0.0	0.0	1.0 0	.0 0.0	0.0 (12F5	5.0) xNUNIT
Line	Symmetry (x') (C	nk. 0.0 0.0 operations CK(1)CK(2)	1.0 0	.0 0.0 CK(3)	0.0 (x)	1.0 0 (CK	.0 0.0 (10))	0.0 (12F5	5.0) xNUNIT
Line	$\begin{array}{rrr} \text{remain blar}\\ 10 1.0 0.0\\ \text{Symmetry}\\ (x') (C\\ (y') = (C) (C) $	nk. 0.0 0.0 operations CK(1)CK(2) CK(4)CK(5)	1.0 0	CK(3) CK(6)	0.0 (x) (y)	1.0 0 (CK +(CK	.0 0.0 (10)) ((11))	0.0 (12F5	5.0) xNUNIT
Line	Lattice contraction remain blan $10 \ 1.0 \ 0.0$ Symmetry (x') (C (y') = (C (z') (C	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8)	1.0 0	CK(3) CK(6) CK(9)	0.0 (x) (y) (y) (y)	1.0 0 (CK +(CK (CK	(10)) (11)) (12))	0.0 (12F5	5.0) xNUNIT
Line	remain blan 10 1.0 0.0 Symmetry (x') (C (y') = (C (z') (C When CK(operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) 1)≥10.0, pro	1.0 0. ceed to	CK(3) CK(6) CK(9) o the nex	(x) (x) (y) (y) (y) (z) (xt line.	1.0 0 (CK +(CK (CK	(10)) (11)) (12))	0.0 (12F5	5.0) xNUNIT
Line	Lattice contraction remain blat $10 \ 1.0 \ 0.0$ Symmetry (x') (C (y') = (C (z') (C When CK(11	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) 1)≥10.0, pro 120 1	1.0 0. ceed to 10	CK(3) CK(3) CK(6) CK(9) the nex (515	(x) (x) (y) (y) (y) (z) (xt line.)	1.0 0 (CK +(CK (CK	.0 0.0 (10)) ((11)) (12))	0.0 (12F5	5.0) xNUNIT
Line	Lattice configuration remain blan $10 \ 1.0 \ 0.0$ Symmetry (x') (C (y') = (C (z') (C When CK(11 120: The n 120: The n	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) 1)≥10.0, pro 120 1 umber of or	1.0 0 ceed to 10 bitals o	CK(3) CK(6) CK(6) CK(9) the new (515) on a mo	(x) (x) (y)(x) (y) (y) (y) (x) (x) (x) (x) (x) (x) (x) (x) (x) (x	1.0 0 (CK +(CK (CK This	(10)) (11)) (12)) numbe	0.0 (12F5	5.0) xNUNIT be the same as
Line Line	remain blat 10 1.0 0.0 Symmetry (x') (C (y') = (C (z') (C When CK(11 120: The n that calcula	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, pro 120 1 umber of or umber of or	ceed to 10 bitals o DH (1).	CK(3) CK(3) CK(6) CK(9) the ney (515 on a mo	(x) (x) (y) (y) (y) (y) (z) (x) (z) (x) (z) (z) (z) (z) (z) (z) (z) (z) (z) (z	1.0 0 (CK +(CK (CK This	(10)) (10)) (11)) (12))	0.0 (12F5	5.0) xNUNIT be the same as
Line Line	remain blat remain blat 10 pm 1.0 pm 0.0 Symmetry (x') (C (y') = (C (z') (C When CK(11 120: The n that calcula 1: Coeffic	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, pro 120 1 umber of or tred in EXTI ients of or	ceed to 1.0 0 10 bitals o DH (1). ne mol	CK(3) CK(3) CK(6) CK(9) the new (515 on a mo	wne 0.0 (x) (y) (y) (y) (z) (t line.) lecule. is read	1.0 0 (CK +(CK (CK This d from	(10)) (11)) (12)) numbe	0.0 (12F5 er should 0. If	5.0) xNUNIT be the same as there are two
Line	remain blan remain blan $10 ext{ 1.0 } ext{ 0.0}$ Symmetry $(x') ext{ (C}$ $(y') = ext{ (C}$ $(z') ext{ (C}$ When CK(11 120: The n that calcula 1: Coeffic independen	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, pro 120 1 umber of or ited in EXTI ients of or at molecule,	<pre>c, d, p, 1.0 0 ceed to 10 bitals o DH (1). ne mol change</pre>	CK(3) CK(6) CK(6) CK(9) the nex (515 on a mo	wne 0.0 (x) (y) (y) (y) (z) (xt line.) lecule. is read e to	1.0 0 (CK +(CK (CK This d from	(10)) (11)) (12)) numbe n fort.1	0.0 (12F5 er should 0. If	5.0) xNUNIT be the same as there are two
Line	remain blat remain blat 10 pm 1.0 pm 0.0 Symmetry (x') (C (y') = (C (z') (C When CK(11 120: The n that calcula 1: Coeffic independen 120	istants: a, b, nk. 0.0 0.0 operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, pro 120 1 umber of or ited in EXTI ients of or at molecule, 2 10	ceed to 1.0 0 10 bitals o DH (1). ne mol change 20.	CK(3) CK(3) CK(6) CK(9) the nex (515 on a molecule	(x) (x) (y) (y) (y) (z) (z) (z) (z) (z) (z) (z) (z	1.0 0 (CK +(CK (CK This d from	(10)) (10)) (11)) (12)) numbe	0.0 (12F5 er should 0. If	5.0) xNUNIT be the same as there are two
Line	remain blan remain blan 10 pm 1.0 pm 0.0 Symmetry (x') (C (y') = (C (z') (C When CK(11 120: The n that calcula 1: Coeffic independen 120 After the N	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, pro 120 1 umber of or ted in EXTI ients of or at molecule, 2 10 CELL mol	1.0 0 1.0 0 1.0 1.0 10 bitals o DH (1). ne mol change 20. ecules	CK(3) CK(3) CK(6) CK(9) the new (515 on a mo ecule	wne 0.0 (x) (y) (y) (y) (z) (xt line.) lecule. is read e to d from	1.0 0 (CK +(CK (CK This d from	(10)) (11)) (12)) numbe n fort.1	0.0 (12F5 er should 0. If 20 ,etc, t	5.0) xNUNIT be the same as there are two hese molecules
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Line	remain blan remain blan $10 ext{ 1.0 } 0.0$ Symmetry $(x') ext{ (C} (y') = ext{ (C} (y') = ext{ (C} (y') + ext{ (C} (y')) = ext{ (C} (y') + ext{ (C} (y')) = ext{ (C} (y')) = ext{ (C} (y') + ext{ (C} (y')) = ext{ (C} (y') + ext{ (C} (y')) = ext{ (C} (y')) = ext{ (C} (y') + ext{ (C} (y')) = ext{ (C} (y')) = ext{ (C} (y') + ext{ (C} (y')) = ext{ (C} (y'$	operations CK(1)CK(2) CK(4)CK(5) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, produced 120 1 umber of or 120 1 umber of or 120 1 10 120 1 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10	1.0 0 1.0 0 1.0 0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.	CK(3) CK(6) CK(6) CK(9) the nex (515 on a mo ecule this lin are read netry of from unit ce (3F5.((x) (x) (y) (y) (y) (z) (z) (z) (z) (z) (z) (z) (z	1.0 0 (CK +(CK (CK This d from fort.10 ons giv 0, the ains N((10)) (10)) (11)) (12)) numbe n fort.1 0, fort.2 ven in total nu CELL x	er should 0. If 20 ,etc, t Line 10 mber of NUNIT	5.0) xNUNIT be the same as there are two hese molecules). If NUNIT f molecules are molecules.
Line Line	remain blat remain blat 10 pm 1.0 pm 0.0 Symmetry (x') (C (y') = (C (z') (C When CK(11 120: The n that calcula 1: Coeffic independen 120 After the N are duplica symmetry NCELL x N 12 0. Translation	operations CK(1)CK(2) CK(4)CK(5) CK(7)CK(8) $1)\geq 10.0$, prodiced in EXTI ients of order the theorem of the theorem	<pre>c, c, c, p, 1.0 0 1.0 0 ceed to 10 bitals o DH (1). ne mol change 20. ecules c symm ure read hen the 0.0 ied to th </pre>	CK(3) CK(3) CK(6) CK(9) the nex (515 on a mo ecule this lin are read netry of from unit ce (3F5.0 he mole	wne 0.0 (x) (y) (y) (y) (z) (t line.) lecule. is read e to d from peratic Line 1 ll conta)) scules i	1.0 0 (CK +(CK (CK This d from fort.10 ons giv 0, the ains N(n Line	(10)) (10)) (11)) (12)) numbe n fort.1 0, fort.2 ven in total nu CELL x 11.	er should 0. If 20 ,etc, t Line 10 NUNIT	5.0) xNUNIT be the same as there are two hese molecules). If NUNIT f molecules are molecules.
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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)₂I₃.

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 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 5205 0.0 1.0 0.0 0010 1.0 -1.0 0.0 0400 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 3 0.0 1.0 0.0 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 (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 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 q2 q1 с 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 (3F10.0) 0.0 0.0 0.0 Translation that specifies the neighboring cell. Line 7 0 3 3 0 (30I2) This means a matrix like: 0 3

3 0

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 > 10.0appears, 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

> 3 0

0

3

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

5 0 2

5.

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 0.

1

This translation generates F, so that form 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. 4

0

[011] 1001 а

0 0

3 Line 8 2 1 20 -25 1 0.0 (6I5, F10.0) 2: Horizontal axis of the map and the drawing of the Fermi surface is $k_{\rm b}$ -axis. 1: Vertical axis of the map and the drawing of the Fermi surface is k_a -axis. 3: Section of the map is $k_{\rm C}$ -axis. 20: The mesh of the horizontal axis is 20. Then the map is calculated from $k_b =$ 0.0 to $k_{\rm b} = \pi/b$ with the interval of $\pi/20b$. -25: The mesh of the vertical axis is 25. Then the map is calculated from $k_a =$ $-\pi/b$ to $k_a = \pi/b$ with the interval of $\pi/25a$. 1: The mesh of the k_c -axis is one, Then the map is calculated only at $k_c = 0.0$. 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 9 0.02 -0.5 0.5 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 1 (I1) Draw the energy band diagram, when 1. Not draw when 0. Line 11 0 10 0.0 0.0 0.0 (2I5, 3F10.0) 0 5 1.0 -1.0 0.0 Instruction for drawing the energy band diagram. The program calculates the energy band from the Γ point (0.0, 0.0, 0.0) to (π/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, 1 5 1.0 -1.0 0.0 1.0 0.0 0.0 3 0.0 this means the crossing point of the lines going through $(\pi/a, -\pi/b, 0.0)$ and $(\pi/a, -\pi/b, 0.0)$ 0.0, 0.0), then the V point in Figure 2. The final "3 0.0" stands for $k_z = 0.0$ 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 the the 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

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

range, change the limits of Line 8.

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 φ ".

(1) The content of planea.dat is as follows:

5	99	6	0 0	(BED	T-TTE	F)2KH	G(SCI	N)4	298 K		
14	1										
10.0	82	20.5	65	9.93	3	103.	700	90.	91	93.0	60
2	0.9	730	0.4	678	0.48	860		С5 В			
2	1.02	270	0.5	321	0.53	140		С6 В			
1	1.03	346	0.4	056	0.5	562		S3 B			
1	1.1	668	0.5	576	0.62	244		S5 B			
1	0.83	332	0.4	424	0.3	756		S4 B			
1	0.90	654	0.5	944	0.4	438		S6 B			
1	0.95	500	0.2	615	0.48	877		S1 B			
1	1.29	964	0.6	917	0.71	182		S7 B			
1	0.70	036	0.3	083	0.28	818		S2 B			
1	1.05	500	0.7	385	0.51	123		S8 B			
2	0.92	206	0.3	413	0.4	650		СЗ В			
2	1.1	682	0.6	410	0.63	163		C8 B			
2	0.83	318	0.3	590	0.38	837		С4 В			
2	1.0	794	0.6	587	0.50	350		С7 В			
5											
1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0	1.0	0.0
1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	1.0	0.0	0.0
20.0											
1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0
1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0	0.0	1.0
2	0.4	581	0.4	696	0.24	450		C5			
2	0.5	133	0.5	337	0.2	/95		C6			
1	0.18	381	0.3	082	0.2	/21		S1			
1	0.54	479	0.7	381	0.4	951		S'/			
1	0.44	470	0.2	641	0.04	401		S2			
1	0.78	392	0.6	912	0.24	423		S8			
1	0.3	146	0.4	431	0.3	183		S3			
1	0.4	508	0.5	964	0.40	087		S5			
Ţ	0.52	254	0.4	085	0.1	165		S4			
Ţ	0.6	525	0.5	583	0.1	9/8		S6			
2	0.3.	194 604	0.3	588 500	0.22	293		C3			
2	0.50	094	0.6	592	0.38	594		C8			
2	0.4.	⊥ / ⊥ ⊂ 1 1	0.3	43U 404	U.1.	369		C4			
2	0.60	ο⊥⊥	0.6	424	0.2	920		C7			

99 Line 1 5

6 5: Input file number that is opened as "planea.dat". (3I4)

99: Not used.

6: Output file number that is opened as "padat.d1".

1

Line 2 14

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.

(2I4)

Line 3 10.082 20.565 9.933 103.700 90.91 93.060 (6F10.5)

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

Line 4 2 0.9730 0.4678 0.4860 (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 6 1.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 1.0 0.0 (12F6.0)

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))

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 $CK(1) \ge 20.0$, and new atomic coordinates are read after the input of Line 6. After once $CK(1) \ge 20.0$ 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.