

EXTDH

Extended Hückel Molecular Orbital Calculation for a Single Molecule

This program calculates molecular orbitals for a discrete single molecule by the extended Hückel method.

Input data: extdh.dat
Source: extdh.f
Indy: extdh.out
PC: extdh

This program generates the following output files:

Output: hdat.d1
Coefficients: fort.xx

Test Data

The supplied input files are for $1-(\text{BETS})_2\text{FeCl}_4$.

(1) Download executable programs suitable for your computer and the following input files.

extdh.A.dat input dat for donor A in $1-(\text{BETS})_2\text{FeCl}_4$
extdh.B.dat input dat for donor B in $1-(\text{BETS})_2\text{FeCl}_4$
extdh.Fe.dat input dat for FeCl_4^- in $1-(\text{BETS})_2\text{FeCl}_4$

(2) Change the filename extdh.A.dat to extdh.dat. This is for the A BETS molecule.

(3) Run extdh. This program generates hdat.d1 and fort.10.

(4) Open hdat.d1 and confirm that the calculation is normally ended.

(5) Change the filename hdat.d1 to hdat.d2, extdh.dat back to extdh.A.dat, and extdh.B.dat to extdh.dat.

(6) Run extdh. This program generates new hdat.d1 and fort.20. Open hdat.d1 to see the calculation is OK.

Input Data

The following is an example of input data in extdh.dat.

```
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 "hdat.d1".

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

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.

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

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

Line 4 1 0.4663 -0.2595 0.4475 (I4, X, 3F10.5) x26
Atom species defined by Line 6 and its x, y, and z coordinates. Atom names are not used inside, but are recommended to be written for your memory.

Line 5 One blank line

Line 6 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 7 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 z, and
-1.47 is ionization potential in Ryd (-13.6 eV).
These values are taken from the previous literatures.¹⁻³ z = 0.0 means double or triple zeta, and requires the next Line 7'.

Line 7' (I4, X, 6F10.5) only when z = 0.0.

Double z : 2 z 1 c1 z 2 c2
Triple z : 2 z 1 c1 z 2 c2 z 3 c3

Line 8 One blank line

Repeat Lines 6 - 8 with the number of atom species. Other Hückel parameters are available from
<http://www.op.titech.ac.jp/lab/mori/EHTB/EHTB~1.html>

Line 9 0 48 0 10 (4I5)
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 96.0 (F4.0)

The number of total electrons.

Line 11 1.75 0.01 1 (3F10.0)

Coefficient of extended Hückel equation. Usually 1.75.

Line 12 1 (I5)

Number of iterations. Usually 1.

For Your Own Crystal

(1) Before editing the input data, 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

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) For the user of teXsan on Indy, the format of atomic coordinates is transformed by trmo. Run trmo, which reads atomic coordinates from atoms dat, and generates at.dat. Copy at.dat and extdh.dat together as

```
%cat extdh.A.dat at.dat >>extdh.dat
```

and move the atomic coordinates to the appropriate place. For other machines, follow this example.

Before doing this, calculate positions of hydrogen atoms (see Appendix). If there is a molecule located on an inversion center or other symmetry operations, make the complete molecule before changing the format.

Editing extdh.dat

- (1) Start an editor to open extdh.dat.
- (2) Change the lattice constants.
- (3) Delete the old atomic coordinates (Line 4).
- (4) Write new atomic coordinates. Move the new atomic coordinates which are attached at the end of the file, to the proper position. If the atom numbering is inappropriate, change the atom species. When there are more than two independent molecules, calculate for the first molecule, and after that move the coordinates of the second molecule to the proper position, and repeat the calculation.
- (5) Change the total number of electrons, if the donor is not BEDT-TTF.
- (6) Save and end "mull".
- (7) Run the program.

Output

Open the output file hdat.d1, and check the following points.

- 1) The energy level of HOMO (48th level) must be 9.2 ± 0.1 eV for BEDT-TTF.
- 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) Open the molecular orbital coefficient file fort.10, and check all sulfur orbitals have the same sign and the symmetry of HOMO is appropriate. 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 $2s$, $2p_y$, $2p_z$, $2p_x$ for each carbon.

For band calculation, repeat the calculation for each crystallographically independent molecule. For example, $1-(\text{BETS})_2\text{FeCl}_4$ has two crystallographically independent molecules A and B.

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

Appendix: Calculation of Hydrogen Atoms

Usually reported data of x-ray crystal structure analysis do not contain atomic coordinates of hydrogen atoms. Here is described the method of calculating atomic coordinates of hydrogen atoms by using texsan.

- (1) Start texsan session of your crystal.
- (2) Open [Parameters][Cell Parameters], and enter the lattice constants.
- (3) Open [Parameters][Space group], and select the space group.
- (4) Open [Model][Menu edit], and enter [Atom name] and the coordinates [x], [y], and [z]. After one atom is entered, push [Next] button, and enter the next atom. It is not necessary to input the anion atoms.
- (5) When you have entered all non-hydrogen atoms, [Exit] the menu edit session.
- (6) Open [Model][Graphics edit], and the entered molecule is displayed. You can rotate the molecule by the scales on the upper left. If coordinates of some atoms are not correct, please correct them by opening [Model][Menu edit] again. Make sure that the coordinates construct the whole molecule. In some analyses some part of the molecule may be included in the next cell, and a molecule is divided by two. In other case a molecule is located on some symmetry operation, and the coordinates of one half of the molecule are given. In that case select [symmetry expansion], and make the whole molecule. Remember how many molecules are crystallographically independent, and in which molecule each atom is included.
- (7) To calculate the positions of the hydrogen atoms, select [geometry]. In case of ethylene part of BEDT-TTF, click [tetrahedral (2 atoms) methylene], and in the figure click the carbon atoms to which the hydrogen atoms are attached, and push [apply].
- (8) Push yellow [Save] bottom to save the calculated coordinates.
- (9) [Quit] the graphics edit session, and finish the texsan by selecting [File][Exit].
- (10) The atomic coordinates processed by texsan is stored in "atoms.dat". By running a data convert program trmo, the format of the coordinates are converted and written on "at.dat".