MOMAP

Tutorial 04

Transport Calculation

MOMAP

Molecular Material Property Prediction Package

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MOMAP Tutorial 04

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MOMAP Tutorial

- Transport Calculation

Interest in charge-carrier drift mobilities in **naphthalene** single crystal has been stimulated by the discovery that the electron mobilities in the b and c' directions are independent of temperature down to about 100 K, below which they increase markedly. This increase is consistent with a transition from hopping to band transport expected from general principles.

Here we use naphthalene single crystal as an example to show how to calculate the charge-carrier mobilities by using the MOMAP **Transport** sub-package.

The basic steps involved in the calculations are as follows:

1. Prepare crystal file
2. Prepare momap.inp
3. Do transport calculations

Contents

Transport Calculations

Prepare Crystal File

First prepare the naphthalene single crystal file, in either mol or cif format, however, the cif format is prefered as it contains the lattice information. Once the crystal file is obtained, we create a directory `naphthalene` as working directory.

The naphthalene input file (`naphthalene.cif`) is as follows:

```
data_naphthalene
_audit_creation_date                  2019-05-20
_audit_creation_method                'Materials Studio'
_symmetry_space_group_name_H-M        'P1'
_symmetry_Int_Tables_number           1
_symmetry_cell_setting                triclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
_cell_length_a                    8.0980
_cell_length_b                    5.9530
_cell_length_c                    8.6520
_cell_angle_alpha                 90.0000
_cell_angle_beta                 124.4000
_cell_angle_gamma                 90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
C1     C   0.082321   0.018562   0.328357  0.00000  Uiso   1.00
C2     C   0.112956   0.163833   0.222892  0.00000  Uiso   1.00
C3     C   0.047989   0.105174   0.037135  0.00000  Uiso   1.00
C4     C   0.076558   0.251823  -0.075824  0.00000  Uiso   1.00
C5     C  -0.013196  -0.190207   0.254606  0.00000  Uiso   1.00
H6     H   0.124192   0.058895   0.455393  0.00000  Uiso   1.00
H7     H   0.178710   0.305594   0.271107  0.00000  Uiso   1.00
H8     H   0.141804   0.390694  -0.023603  0.00000  Uiso   1.00
H9     H  -0.033302  -0.295196   0.331298  0.00000  Uiso   1.00
C10    C  -0.047989  -0.105174  -0.037135  0.00000  Uiso   1.00
C11    C  -0.112956  -0.163833  -0.222892  0.00000  Uiso   1.00
……
C28    C   0.547989   0.394826   0.037135  0.00000  Uiso   1.00
C29    C   0.612956   0.336167   0.222892  0.00000  Uiso   1.00
C30    C   0.582321   0.481438   0.328357  0.00000  Uiso   1.00
C31    C   0.576558   0.248177  -0.075824  0.00000  Uiso   1.00
C32    C   0.486804   0.690207   0.254606  0.00000  Uiso   1.00
H33    H   0.624192   0.441105   0.455393  0.00000  Uiso   1.00
H34    H   0.678710   0.194406   0.271107  0.00000  Uiso   1.00
H35    H   0.641804   0.109306  -0.023603  0.00000  Uiso   1.00
H36    H   0.466698   0.795196   0.331298  0.00000  Uiso   1.00
```

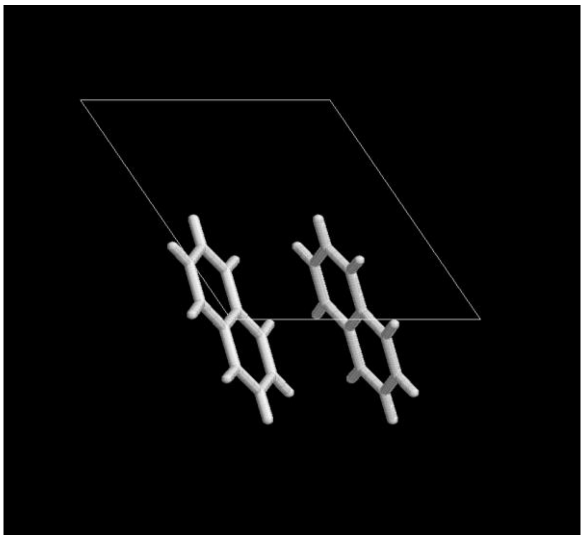


Fig. 1 Naphthalene unit cell

It is clear that the cif file is an output of Materials Studio with space group of 'P1', currently MOMAP Transport program can support all space groups, not restricted only to space group 'P1'. With a cif file, we have all the crystal structure parameters in hand, as shown above.

Prepare momap.inp

Now we have prepared our crystal file, however, before we can run the MOMAP Transport calculations, we have to prepare the `momap.inp` file, a control file for MOMAP package.

There exist quite a few of control parameters for `momap.inp`, however, all the parameters have their default values if we do not set them. To make life easy, we have written a program called `transport_geninp.exe` to generate the `momap.inp` for the MOMAP transport calculations.

Before we begin to generate the `momap.inp`, we would better setup our environment settings, as these settings rarely change in a specific computing cluster environment. The typical environment settings are as follows (you can put them in `~/.bashrc`, for example):

```
export MOMAP_JOB_SCHED=slurm
export MOMAP_JOB_QUEUE=X12C
export MOMAP_QC_EXE=g09
export MOMAP_QC_PPN=12
export MOMAP_MODULE_QC=gaussian/g09.e01
```

These are the initial values that will be entered into our `momap.inp` if we run the `transport_geninp.exe`, we can change them later on with an editor. The currently supported scheduling systems include PBS, SLURM, LSF and LOCAL, these are the scheduling systems in frequent use. The LOCAL means the jobs are run in a local machine, it can be of great help for a linux box without job scheduling system, for example. If needed, more scheduling systems can be added.

If the computing cluster is installed with environment module, the last two lines can be added, but we can change the contents according to our specific situation.

If our quantum calculation (QC) engine is of the Gaussian g16, we need to change the third line to g16, and the fifth line to g16.b01, for example.

Once the MOMAP environments are set, we can use our `transport_geninp.exe` to generate `momap.inp`, all the MOMAP Transport programs have a help option, either `-h` or `--help`, for example, in case `transport_geninp.exe`, we have:

```
[test1]$ transport_geninp.exe --help
*******************************************************************
*   MOMAP Transport Calculation Utility                           *
*   Zhigang Shuai Group, Dep. of Chem., Tsinghua Univ., Beijing   *
*******************************************************************
Transport Input Generation

Usage: transport_geninp.exe [opts]
     -config momap.inp  : set config file, default to momap.inp
     -cif               : use cif file as molecule input (default)
     -mol               : use mol file as molecule input
     -module            : set to use environment module flag
     -terse             : generate terse momap.inp (default)
     -verbose           : generate verbose momap.inp

e.g.: transport_geninp.exe
     transport_geninp.exe -config momap.inp
     transport_geninp.exe -verbose
     transport_geninp.exe -cif
     transport_geninp.exe -mol
     transport_geninp.exe -module
     transport_geninp.exe -config momap.inp -verbose
```

If option `-config` is used, then we can designate our output control file, the default file is `momap.inp` if this option is not specified.
If option `-cif` is used, then cif crystal parameter will be used in `momap.inp`, it will automatically search for the first found cif file in the current directory if it exists.
If option `-mol` is used, then mol molecule parameter will be used in `momap.inp`, again it will automatically search for the mol files in the current directory.
If option `-module` is used, then it will activate module parameter output.
If option `-terse` is used, then it will generate a *terse* `momap.inp`, while the other parameters using the default values.
If option `-verbose` is used, then it will generate a *verbose* `momap.inp`, almost all the parameters will be entered into the `momap.inp`. Thus, we can tune the parameters as needed.

These options can be used in combination, as shown in the last line.

If we run the `transport_geninp.exe` without any options, it will generate a `momap.inp` like the following:

```
[naphthalene]$ cat momap.inp
&transport
  do_transport_prepare             = 1
  do_transport_submit_HL_job       = 1
  do_transport_get_transferintegral= 1
  do_transport_submit_RE_job       = 1
  do_transport_get_re_evc          = 1
  do_transport_run_MC              = 1
  do_transport_get_mob_MC          = 1
  do_transport_run_MC_temp         = 0
  do_transport_get_mob_MC_temp     = 0
  do_transport_run_ME              = 0
  do_transport_get_mob_ME          = 0
  do_transport_run_ME_temp         = 0
  do_transport_get_mob_ME_temp     = 0
  do_transport_gatherdata          = 1


  # Job Scheduling
  sched_type        = pbs       ! pbs, slurm, lsf, or local
  queue_name        = blade

  compute_engine    = 1         ! 1 = Gaussian, 2 = ORCA, 3 = Q-Chem
  qc_exe            = g09       ! g09/g16 or fullpath/orca or qchem

#  module_qc        = gaussian/g09.e01

  qc_method         = b3lyp
  qc_basis          = b3lyp STO-3g
  qc_basis_re       = b3lyp STO-3g
  qc_memory         = 4096  ! MB
  qc_nodes          = 1
  qc_ppn            = 8

  temp              = 300

  # Temperature Dependence
  start_temp        = 200
  end_temp          = 300
  delta_temp        = 50

  ratetype          = marcus  ! macus or quanta

  lat_cutoff        = 4       ! for neighbor list construction

  nsimu             = 2000
  tsimu             = 1000    ! in ns
  tsnap             = 5

  crystal           = naphthalene.cif
/
```

The MOMAP Transport package uses the following control block:

```
&transport
…
/
```

It starts with `&transport`, and ends with `/`.

The lines beginning with '#' are comments, the '!' is also used for comment as in the case of Fortran coding.

The initial `do_` lines are control flags, can be either 1 (enabled) or 0 (disabled). If we need to do MC calculations, we simply set them to 1 accordingly.

With the generated `momap.inp`, we can do some fine tunings for our specific case, for example, we may change `queue_name` value from `blade` to `X12C`, `gaussian_ppn` from 16 to 12.

In the meantime, a file called `run.sh` is also generated, it contains:

```
[test1]$ cat run.sh
#!/bin/sh

python $MOMAP_ROOT/bin/momap.py &> momap.log &
```

Do Transport Calculations

Once we have carefully checked the `momap.inp`, we can simply run the `run.sh` by issuing:

```
[test1]$ sh run.sh
```

Or

```
[test1]$ python $MOMAP_ROOT/bin/momap.py &> momap.log &
```

In the meantime, we can check the running processes by looking into the `momap.log` file , or the `RUN` directory where the running locks are located. We may also use the job scheduling commands to check the running processes.

If everything is okay, at the end of the log file, with somethings like the following:

```
…
************************************
*      All successfully done.      *
************************************
Duration: 0 days 0 hours 9 minutes 57 seconds.
```

will appear, which means the job is done successfully.

Please carefully check the `momap.log` file for any abnormalities.

Finally, the output results are gathered and put in file `momap-marcus.dat`.

File and Directory Structure

In the process of transport calculations, quite a lot of files and directories are created. The full directory and file tree is shown in the following pages (in Linux case, by simply run the `tree` command):

```
[naphthalene]$ tree ./
./
├── data
│   ├── config.inp
│   ├── H.inp
│   ├── L.inp
│   ├── mol1_bonds.dat
│   ├── mol1.mol
│   ├── mol1_neighbors.cif
│   ├── mol1_trans_int_files.dat
│   ├── mol2_bonds.dat
│   ├── mol2.mol
│   ├── mol2_neighbors.cif
│   ├── mol2_trans_int_files.dat
│   ├── neighbor.dat
│   ├── supercell.cif
│   ├── unique_id_map.dat
│   └── unitcell.cif
├── evc
│   └── mol1
│       ├── elec
│       │   └── job_get_NM.pbs
│       └── hole
│           └── job_get_NM.pbs
├── HL
│   ├── 2mol-11.com
│   ├── 2mol-13.com
│   ├── 2mol-1.com
│   ├── 2mol-5.com
│   ├── 2mol-7.com
│   ├── nei_mol-11.com
│   ├── nei_mol-13.com
│   ├── nei_mol-1.com
│   ├── nei_mol-5.com
│   ├── nei_mol-7.com
│   └── uc_mol-1.com
├── jobs
│   ├── job_2mol.pbs
│   ├── job_nei_mol.pbs
│   ├── job_re-mol1-anion.pbs
│   ├── job_re-mol1-cation.pbs
│   ├── job_re-mol1-neutral.pbs
│   ├── job_transint.pbs
│   └── job_uc_mol.pbs
├── MC-marcus
│   ├── elec
│   │   ├── get_mob.pbs
│   │   ├── get_mob.py
│   │   ├── prepare-mc.py
│   │   ├── run_mc_batch.py
│   │   └── run_mc.pbs
│   └── hole
│       ├── get_mob.pbs
│       ├── get_mob.py
│       ├── prepare-mc.py
│       ├── run_mc_batch.py
│       └── run_mc.pbs
│
```

Cont.

```
├── mol1.mol
├── mol2.mol
├── momap.inp
├── RE
│   ├── evc-e-mol1.inp
│   ├── evc-e-mol2.inp
│   ├── evc-h-mol1.inp
│   ├── evc-h-mol2.inp
│   ├── re-mol1-anion.com
│   ├── re-mol1-cation.com
│   └── re-mol1-neutral.com
├── RUN
├── run.sh
└── scr
    ├── batch_formchk.py
    ├── gaussian_log_check.py
    ├── get_RE.py
    ├── get_transint.py
    ├── mol_one_nei.py
    ├── mol_one_uc.py
    ├── mol_RE.py
    ├── mol_two.py
    ├── momap.sh
    ├── prepare_RE.py
    └── run_RE.py

13 directories, 67 files
```

As we only calculate the ***unique*** molecules and molecular pairs (dipoles), we need to map these unique molecules and molecular pairs to the orginal molecule and molecular pairs, the mapping information is put in file `unique_id_map.dat` under `data` directory:

```
[test1]$ cat unique_id_map.dat
# Unique ID mapping
2
  14
      1   1    1
      1   2    2
      1   3    3
      1   4    4
      1   5    5
      1   6    6
      1   7    7
      1   8    8
      1   9    9
      1  10   10
      1  11   11
      1  12   12
      1  13   13
      1  14   14
  14
      2   1   15
      2   2   16
      2   3   17
      2   4   18
      2   5   19
      2   6   20
      2   7   21
      2   8   22
      2   9   23
      2  10   24
      2  11   25
      2  12   26
      2  13   27
      2  14   28
```

The first line is comment, the 2nd line is the number of molecules in the central unitcell, then follows number of neighbors for each central unitcell molecule and ID mapping data, which repeats the number of molecules in the central unitcell. For the three-column data in the above table, the first column is the central unitcell molecule ID, the second column is the neighbor ID for the corresponding central unitcell molecule, and the third column is the *uniformly* numbered IDs for the whole central unitcell.

Thus, for example, a file `2mol-13.com` has a uniform ID 13, which corresponds to central unitcell molecule ID 1 and neighbor molecule ID 13, as show in the above list. As another example, if we have a file `2mol-24.com`, from the above list, we know it corresponds to the central unitcell molecule ID 2 and neighbor molecule ID 10.

Transfer Integral Calculations

The work is done by calling two python scripts in `scr` directory, that is, `mol_one.py` and `mol_two.py`, to do the one-molecule single point energy calculations and two-molecule single point energy calculations. These two python scripts set up running locks and submit jobs for the transfer integral calculations.

Reorganization Energy Calculations

The work is done by calling a python script in `scr` directory, that is, `mol_RE.py`, to do the reorganiztion energy calculations. The python script sets up running locks and submit jobs for the reorganization energy calculations. Comparing to the transfer integral calculations, this step takes more time to finish.

Collect Transfer Integrals

The work is done by calling the python script `scr/get_transint.py`, we obtain the transfer integral data, such as, VH01.dat, VL01.dat, VH02.dat, VL02.dat *etc*. for the later transfer hopping rate calculations, which are located in the `data` directory.

Analyze Reorganization Energies

To obtain the reorganization energies, we split the calculation into three parts: `prepare_RE.py`, `run_RE.py`, and `get_RE.py`. The first part is to prepare input files for the `evc.exe` program to do normal mode calculations, the second part is use the scheduling system to do the actual calculations, while the third part is to collect the calculated results and put the results into places, for examples, `NM01-e.dat`, `NM01-h.dat` in data directory.

Monte Carlo (MC) simulations

Once the above preparation work is done, we can do MC simulations to calculate the charge carrier motilities.

This step is also split into two parts, that is, `prepare-mc.py` and `run_mc_batch.py`. The first part is to copy the obtained related input files (e.g., VH01.dat, VL01.dat, VH02.dat, VL02.dat, NM01-e.dat NM01-h.dat, NM02-e.dat, NM02-h.dat *etc.*) into the MC working directory, and do the hopping rate calculations. The second part is to submit jobs to the scheduling (batching) system to do the MC simulations. As the MC program runs, the track files are written out into `tracks` directory. Normally, 2000 tracks will generate fairly good mobility results.

In this step, we normally take advantage of the OpenMP parallelization capability, it linearly scales with the number of cores in a node. For example, if the running node has 28 cores, the performance gain is 28 times comparing to the same serial job.

Calculate Random Walk Mobilities

Once the MC simulations finish, we can calculate the random walk mobilities from the MC track files by using the Einstein relationship.

Depends on the `do_` options we selected, there may be temperature dependent MC simulations and mobility calculations, or ME related calculations, for example, but the procedures are similar.

In the MC calculation directories, if the ps2png is properly installed, we can use the following commands to generate and display the 3D and 2D mobility plots:

```
$> gnuplot *.gnu
$> ps2png *.eps
$> display *.png
```

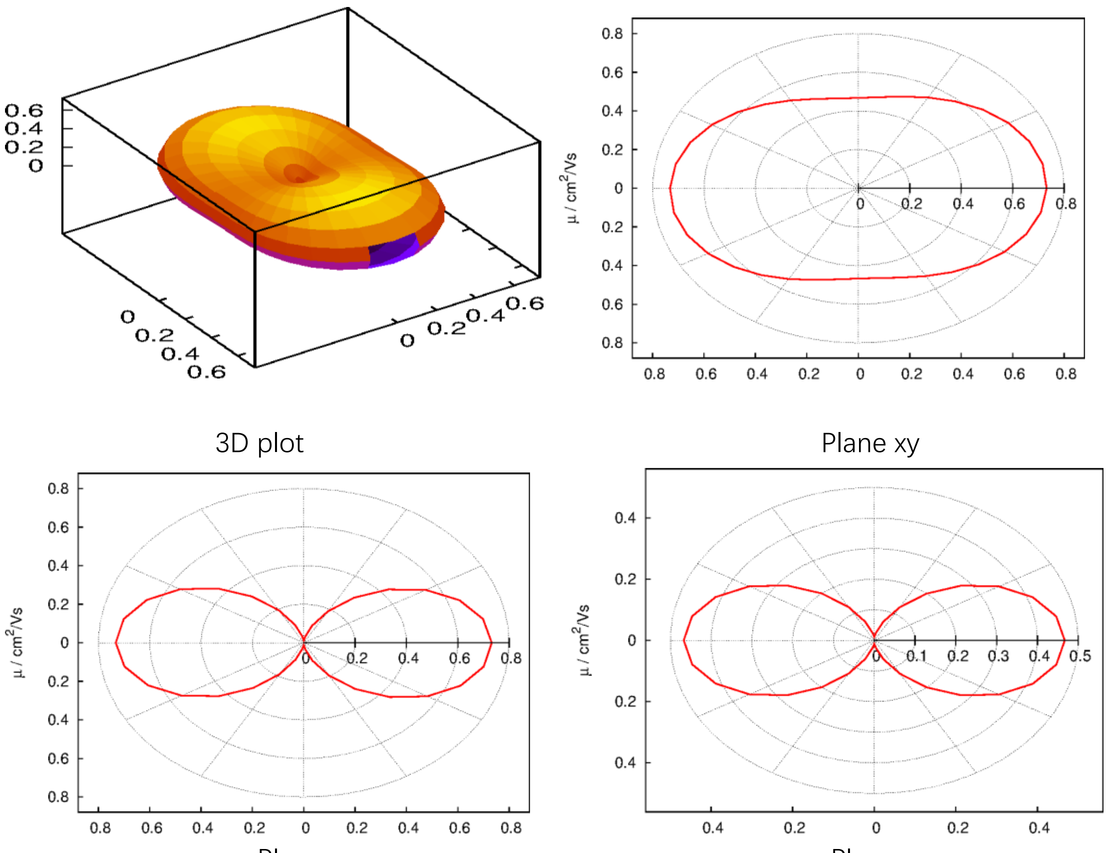
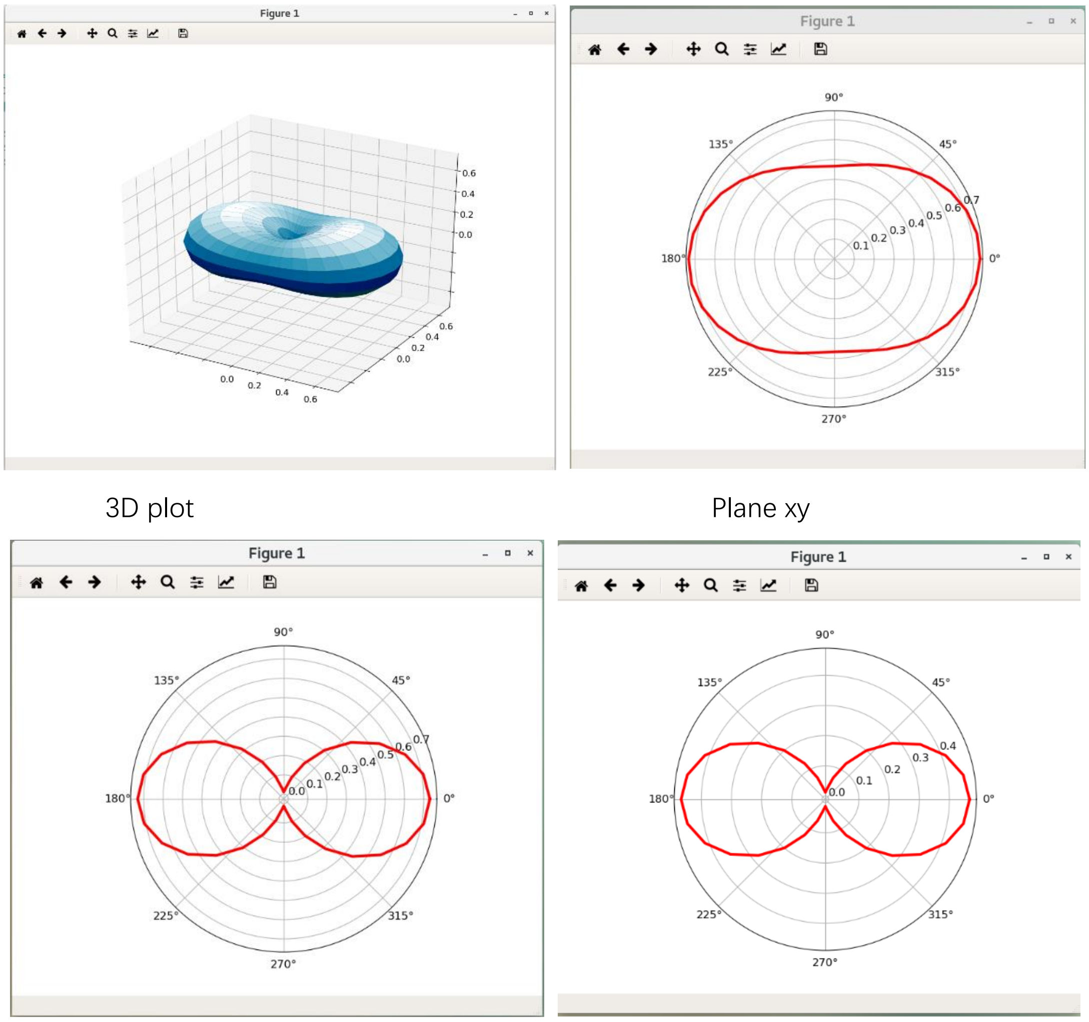


Fig. 10-1 The 3D and 2D plots for the electron case by using gnuplot

In addition, if numpy and matplotlib packages are installed with python, we can also use the generated python scripts to display the mobility plots. The corresponding python scripts in running MC directories are: `mob_direction_all.py`, `mob_plane_xy.py`, `mob_plane_xz.py` and `mob_plane_yz.py`. For examples, the 3D and 2D plots for the electron case are shown as follows:



3D plot

Plane xy

Plane xz

Plane yz

Fig. 10-2 The 3D and 2D plots for the electron case by using matplotlib with python

Gather data

As all the calculations finish, the results are gathered to the file `momap.dat` as follows.

```
  __  __    ___    __  __      _      ____
 |  \/  |  / _ \  |  \/  |    / \    |  _ \
 | |\/| | | | | | | |\/| |   / _ \   | |_) |
 | |  | | | |_| | | |  | |  / ___ \  |  __/
 |_|  |_|  \___/  |_|  |_| /_/   \_\ |_|       Version 2019A (2.0.0)

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        Institute of Chemistry, Chinese Academy of Sciences.
        All Rights Reserved.

Running configuration:
  data/config.inp

Separated molecular information:
  data/mol1.mol
  data/mol2.mol

Neighbor information:
  data/neighbor.dat
  data/mol1_neighbors.cif
  data/mol2_neighbors.cif

Transfer integral information:
  data/VH01.dat
  …

Reorganization energy information:
  data/NM01-e.dat
  …

**** Hopping rates for MC-marcus/elec:
  MC-marcus/elec/w0_01.out
  MC-marcus/elec/w0_02.out

**** Mobility data for MC-marcus/elec
mob_a  / error [cm**2/Vs]:  6.283116e+00   6.268443e-01
mob_b  / error [cm**2/Vs]:  4.462247e+00   4.881686e-01
mob_c  / error [cm**2/Vs]:  8.591702e-06   7.566622e-07
mob_av / error [cm**2/Vs]:  3.581787e+00   1.879785e-01
Directional mobilities are in file:
  MC-marcus/elec/mob_direction_all.dat
**** End of Mobility data for MC-marcus/elec

**** Hopping rates for MC-marcus/hole:
  MC-marcus/hole/w0_01.out
  MC-marcus/hole/w0_02.out

**** Mobility data for MC-marcus/hole
mob_a  / error [cm**2/Vs]:  5.832380e+00   5.140441e-01
mob_b  / error [cm**2/Vs]:  5.071254e+00   4.927727e-01
mob_c  / error [cm**2/Vs]:  7.975353e-06   6.495725e-07
mob_av / error [cm**2/Vs]:  3.634544e+00   2.263642e-01
Directional mobilities are in file:
  MC-marcus/hole/mob_direction_all.dat
**** End of Mobility data for MC-marcus/hole

Normal end of MOMAP data gathering.
```

Finally, the job is done!