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Computational Chemistry Research Group at North Dakota State University

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-Part of the input data for the quantum dynamics are computed based on the third-party software: Vienna Ab Initio Simulation Package (VASP). **A license and access to this software must be obtained independently**. This license does not cover any aspects of use of VASP-software. NDSU can provide recommendations on optimal use of this software or by replacing it by a free alternative software.
-Part of the computational tool package is implemented in the form of scripts under third-party MATLAB software. **A license and access to this software must be obtained independently**. This license does not cover any aspects of use of MATLAB-software. NDSU can provide recommendations on optimal use of this software or by replacing it by a free alternative software.
-Any publications that use the results obtained with the Redfield Computational Tool must cite one of the papers listed below, as the main value of the computational tool is in the idea and algorithm.

D. Micha, JPCL2010; https://pubs.acs.org/doi/10.1021/jz100122f
S. Huang, JCTC 2014, https://pubs.acs.org/doi/10.1021/ct5004093
T. Inerbaev, JPCC 2013; https://pubs.acs.org/doi/10.1021/jp311076w
Y.Han, Mol. Phys 2018
https://www.tandfonline.com/doi/full/10.1080/00268976.2017.1416193
If needed, original papers can be co-cited with more recent reviews on updated methods, listed at the end of the license.

-Any registered user of the computational tool can be provided with codes, manuals, and an informal support line, based on availability of the development team.
-A violation of any of the above conditions will revoke this license.

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Complementary info:

1. Additional references

Jiangchao Chen, JPCL2013, https://pubs.acs.org/doi/10.1021/jz400760h
S. Jensen, JPCC 2016; https://pubs.acs.org/doi/10.1021/acs.jpcc.5b12167
Y. Han, JCTC 2017; https://pubs.acs.org/doi/10.1021/acs.jctc.7b00050
Yulun Han, Mol Phys. 2015: https://www.tandfonline.com/doi/full/10.1080/00268976.2014.944598
J. Vogel, JPCL 2015 https://pubs.acs.org/doi/10.1021/acs.jpcc.5b06434
A.Forde, JPCC2018 https://pubs.acs.org/doi/10.1021/acs.jpcc.8b05392
A. Forde, JCTC 2021 https://pubs.acs.org/doi/10.1021/acs.jctc.1c00691?ref=PDF

Alexei Akimov's Software event: CyberTraining, Nonadiabatic, and such…

STEP	SOFTWARE	EXAPLE FILES	NEEDED INPUT
0.Optimization	= VASP	POSCAR	
1.int. orbitals	= perl	band_integrate_vasp5.pl	
1.Heat	= VASP	INCAR_heat	
2.MD	= VASP	INCAR_MD	
			p001, p002, p003,…
3.couplings	= Fortran	bscipt.sh	input_overlap
		Overlap.f	
4.os. strength	= Fortran	os_strength.f	
5.autocorr.	= MATLAB	coupling.001, coupling.002, coupling.003	
6.inspect list of input files		RRR, bandout, energy_pop, ForMasterOptics	
7.modify input parameters		iE, iH	
8.electronic dynamics	= MATLAB		
9.analyze relaxation rates		Ke, Kh	
10. analyze charge transfer		overlay with atomistic model	
11.analyze photoluminescence		watch for non-Kasha transitions	

SUMMER2022

May 31, 2022, 4:00PM

#1 **Knowledge transfer session. VASP skills and Molecular Dynamics**

RECORDINGS: https://youtu.be/8kwljXKO0mc

June 7th, 2022, 4:00pm

#2 **Knowledge transfer. Nonadiabatic Couplings**

RECORDINGS: https://youtu.be/P5lqMiYVZec

June 14th, 2022, 4:00pm

#3 **Knowledge transfer. Averaging procedure. Convert couplings to Rates. Electron dynamic**

RECORDINGS: https://youtu.be/OTs-oRzooTA

June 21st, 2022, 4pm

#4 **Knowledge transfer. Excited state dynamics of electrons**

RECORDINGS: https://youtu.be/ALTrCitk-mA

June 28th, 2022, 4pm

#5 **Knowledge transfer. Observables extracted from excited state dynamics**

PART A: https://youtu.be/3QhDUgIdhw8

PART B: https://youtu.be/aFUuEZIo1dE

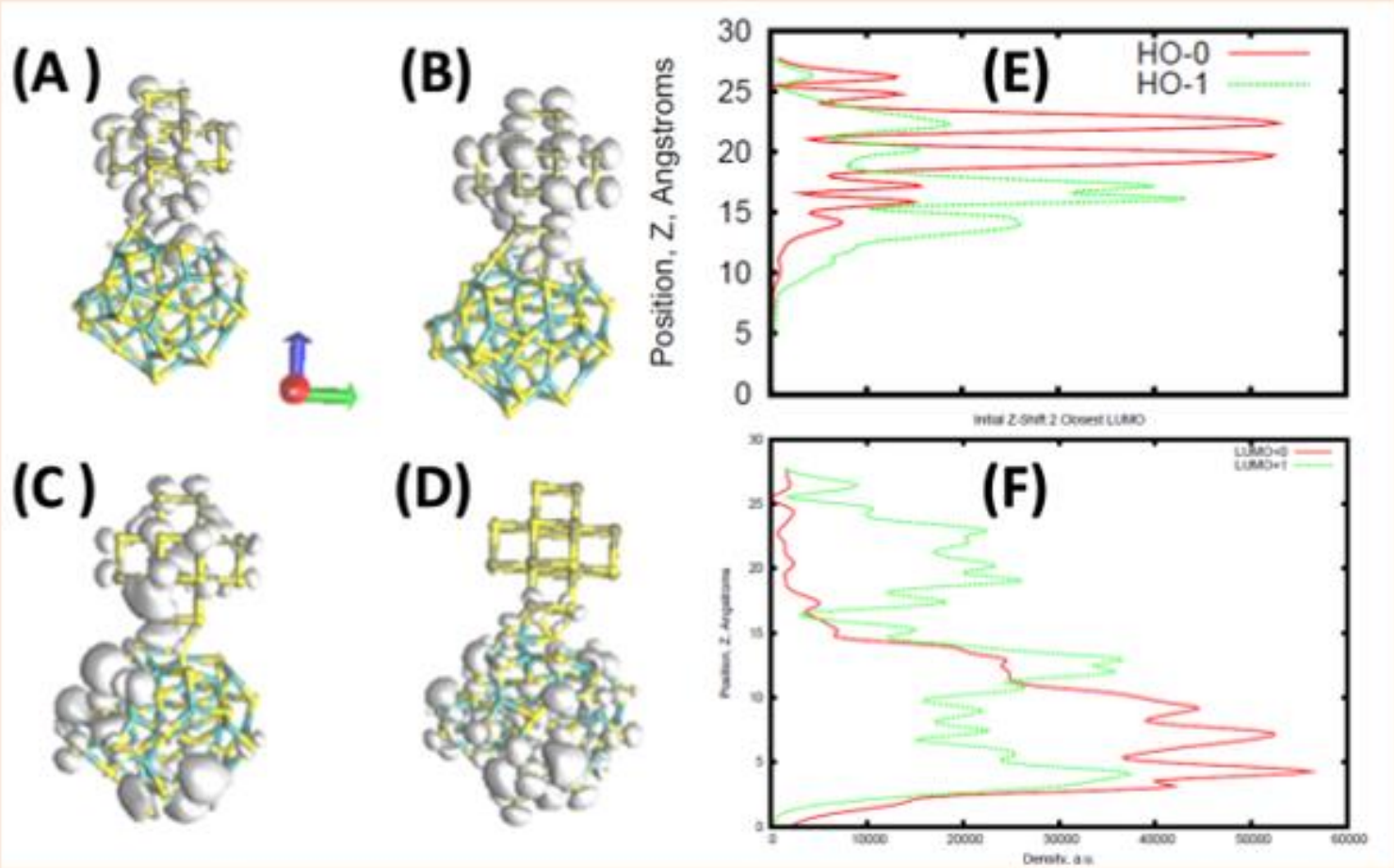
Integration of Electron Orbitals: 3D to 1D

Hadassah B. Griffin

Computational Chemistry Skill Presentation

May 31st, 2022

Overview: 3D vs. 1D Visualization



(A)HOMO – 1
(B)HOMO
(C)LUMO
(D)LUMO + 1
(E)1D Z orbital
HOMO density
(F)1D Z orbital
LUMO density

Background

- Density Functional Theory (DFT): electron density
- Kohn-Sham Orbitals like “band structure” in DFT
- 3D and 1D visualization can help us see if charge transfer occur
- All calculations that followed created with VASP

Files Prepared (PARCHG); Script to Integrate into 1D Orbitals; Output

```
kilin@cori08:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/hgriffin/Project/GROUND_ROT/hybrid_initialZS
hift_2> ls
CHG        OUTCAR             PARCHG.0383.ALLK  WAVECAR                  parch_378.z
CHGCAR     PARCHG.0374.ALLK   PARCHG.0384.ALLK  XDATCAR                  parch_379.z
CONTCAR    PARCHG.0375.ALLK   PARCHG.0385.ALLK  band_integr_V_vasp5.pl   parch_380.z
DOSCAR     PARCHG.0376.ALLK   PARCHG.0386.ALLK  data0                    parch_381.z
EIGENVAL   PARCHG.0377.ALLK   PARCHG.0387.ALLK  data1                    slu 57516068.out
IBZKPT     PARCHG.0378.ALLK   PARCHG.0388.ALLK  debug.sn                 sl 966396.out
INCAR      PARCHG.0379.ALLK   PCDAT            parch_37                 vas .xml
KPOINTS    PARCHG.0380.ALLK   POSCAR           parch_37
LOCPOT     PARCHG.0381.ALLK   POTCAR           parch_37
OSZICAR    PARCHG.0382.ALLK   REPORT           parch_37
kilin@cori08:/glo l/cfs/cdirs/m1251/vasp/CHEM676_2022/ iffin/Project/G D_ROT/hybrid_initialZS
hift_2>
```

Creating 3D Oribitals in NERSC

```
band_integr_V_vasp5.pl
data
```

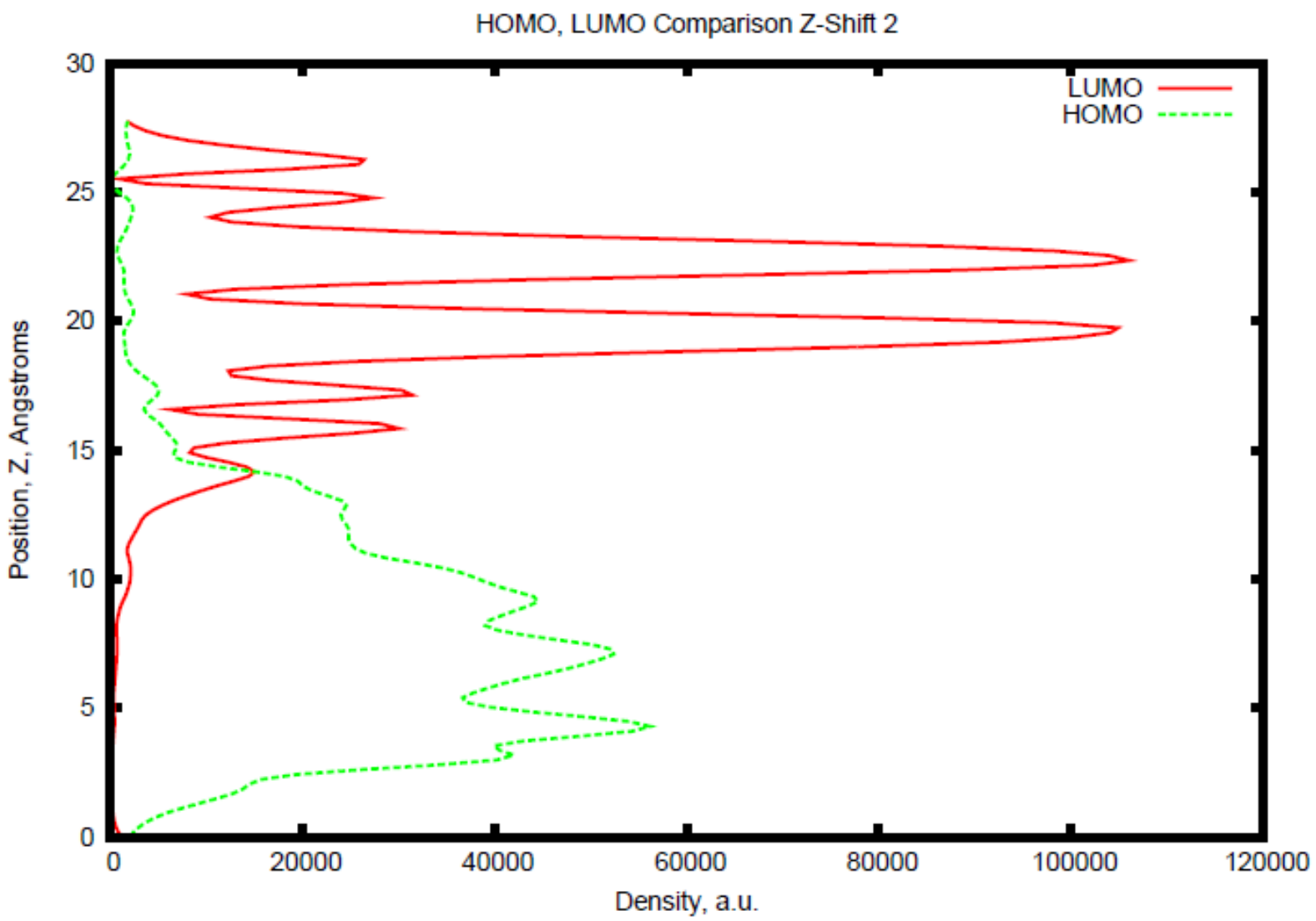
Inputs:
Band orbital number start
Band orbital number finish

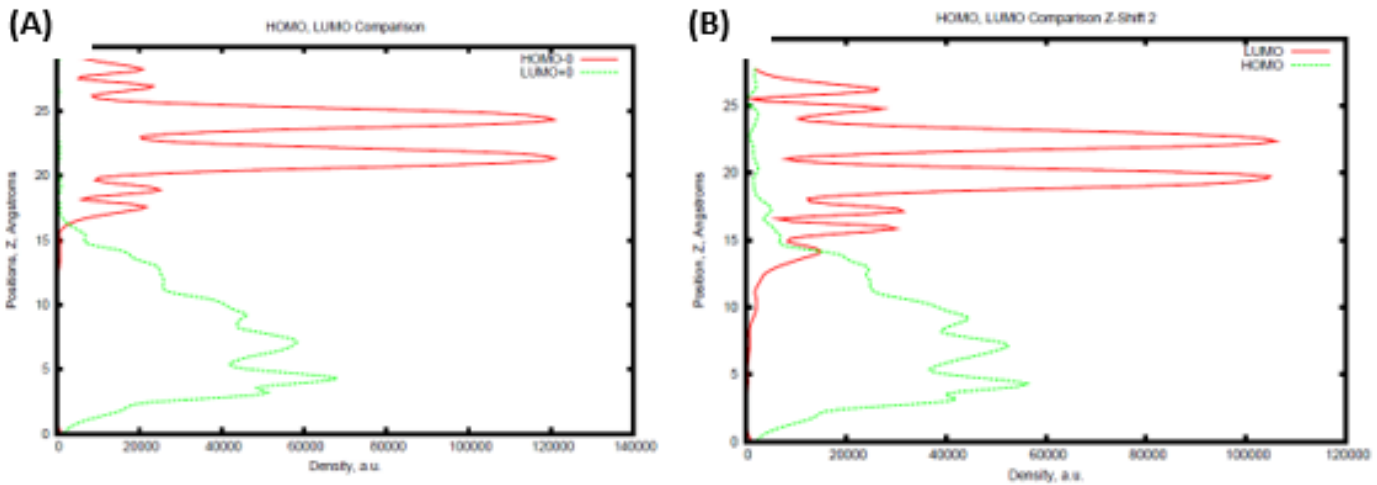
Outputs:
.z files

Another option in NERSC: band_integrate_vasp5.pl
****Will be used in 2-3 weeks for projects***

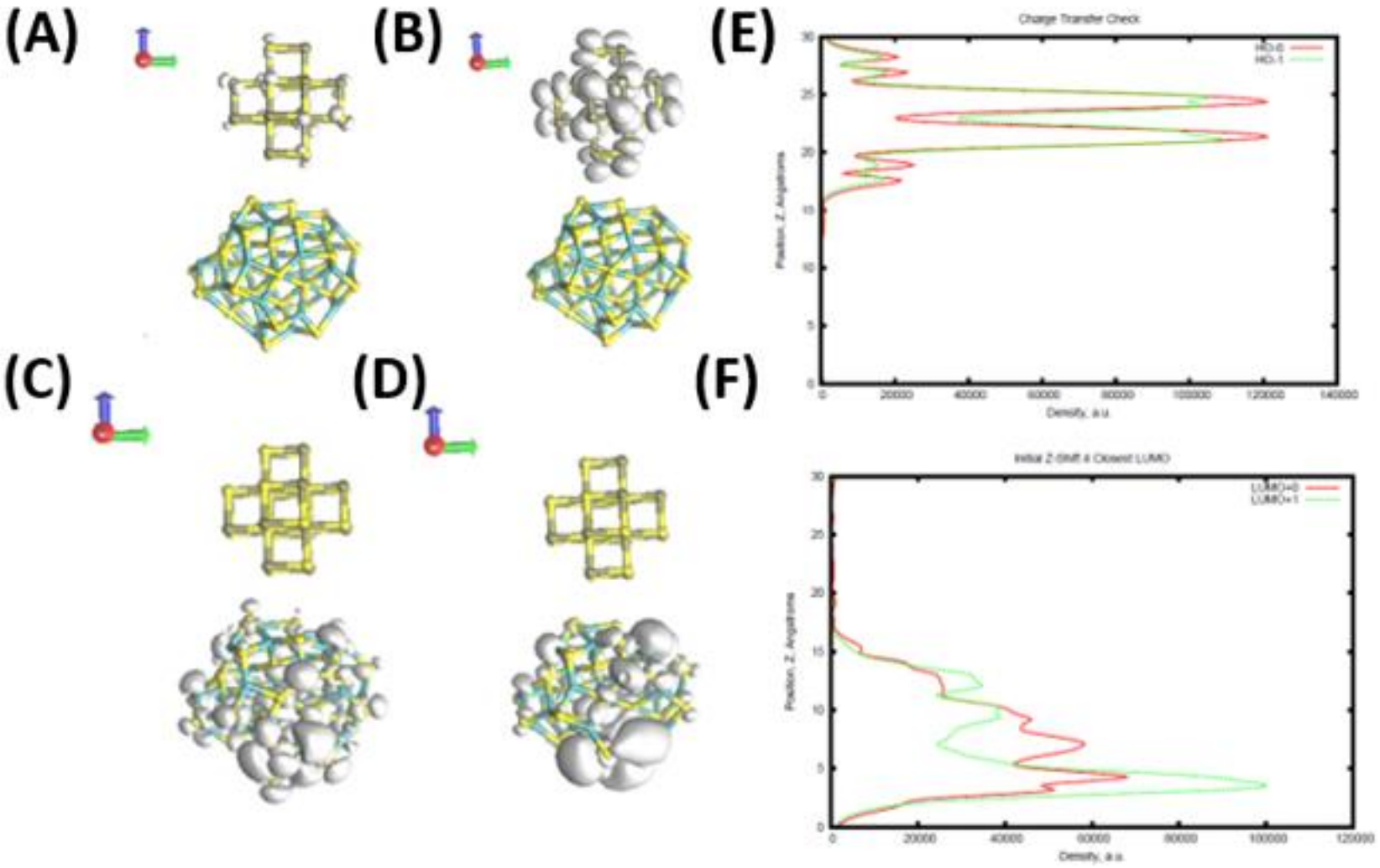
".z" File output below; can plot .z Files in gnuplot; Columns: *position, density, normalized value for you if you want to plot on your own system*

```
kilin@cori08:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/hgriffin/Project/GROUND_ROT/hybrid_initialZS
hift_2> more parch_377.z
0  1185.01593596539  1185.01593596539/2646002.51130121
 0.18634012  830.411548848296  830.411548848296/2646002.51130121
 0.37268024  592.457553228192  592.457553228192/2646002.51130121
 0.55902036  440.328034187658  440.328034187658/2646002.51130121
 0.74536048  339.757970483286  339.757970483286/2646002.51130121
 0.9317006  265.855079098652  265.855079098652/2646002.51130121
 1.11804072  225.959061542117  225.959061542117/2646002.51130121
 1.30438084  204.663884369326  204.663884369326/2646002.51130121
 1.49072096  181.838186221988  181.838186221988/2646002.51130121
 1.67706108  171.872816168954  171.872816168954/2646002.51130121
 1.8634012  171.002833831824  171.002833831824/2646002.51130121
 2.04974132  164.163587880794  164.163587880794/2646002.51130121
 2.23608144  168.368484024643  168.368484024643/2646002.51130121
 2.42242156  187.64643546198  187.64643546198/2646002.51130121
```


HOMO, LUMO Comparison Z-Shift 2
LUMO
HOMO
Position, Z, Angstroms
Density, a.u.
0
5
10
15
20
25
30
0
20000
40000
60000
80000
100000
120000

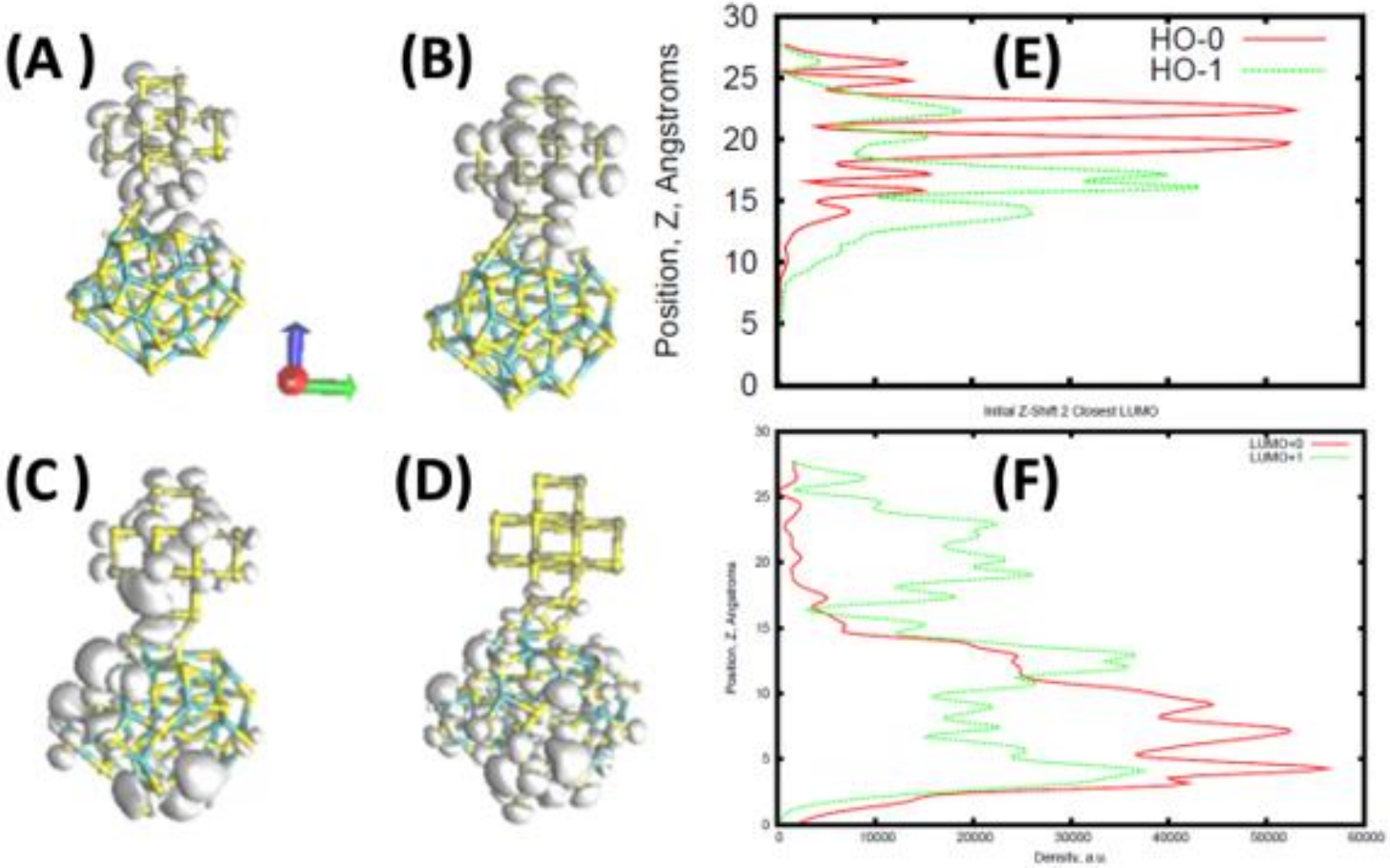

(A)
HOMO, LUMO Comparison
HOMO=0
LUMO=0
Position, Z, Angstroms
Density, a.u.
(B)
HOMO, LUMO Comparison Z-Shift 2
LUMO
HOMO
Position, Z, Angstroms
Density, a.u.

Kohn-Sham Orbital Electron Densities: 3D and 1D Representations, Hybrid Z-Shift 4



(A)HOMO – 1
(B)HOMO
(C)LUMO
(D)LUMO + 1
(E)1D Z orbital HOMO density
(F)1D Z orbital LUMO density

Kohn-Sham Orbital Electron Densities: 3D and 1D Representations, Hybrid Z-Shift 2



(A)HOMO – 1
(B)HOMO
(C)LUMO
(D)LUMO + 1
(E)1D Z orbital HOMO density
(F)1D Z orbital LUMO density

Thermal Heating and standard Molecular Dynamics

Summer 2022 knowledge transfer

Sara Tolba

Heat and MD Equations

$$\sum_{I=1}^{N} \frac{M_I \left(\frac{dR_I}{dt} |_{t=0} \right)^2}{2} = \frac{3}{2} N K_B T$$

where M, and $\frac{dR_I}{dt}$ stand for the mass and initial velocity of Ith nucleus, N is a number of nuclei, K_B is the Boltzmann constant, and T is the temperature. The forces F, are acting on each atom with certain velocity enter the Newton' equation of motion,

$$M_I \frac{d^2 R_I(t)}{dt^2} = F_I(t)$$

To do Molecular Dynamics simulation

Geometry optimized model

Copy from optimization job:
CONTCAR
POTCAR
KPOINTS

Copy from the server:
cp ~/bin/INCAR-heat .

Heating model

Copy from heating job:
CONTCAR
POTCAR
KPOINTS

Copy from the server:
cp ~/bin/INCAR-md .

Molecular dynamics

Ensembles using different Thermostats

	Thermostat			
Ensemble	Andersen	Nose-Hoover	Langevin	Multiple Andersen
NVE	MDALGO=1, ANDERSEN_PROB=0.0			
NVT	MDALGO=1	MDALGO=2	MDALGO=3	MDALGO=13
	ISIF=2	ISIF=2	ISIF=2	ISIF=2
NpT	not available	not available	MDALGO=3	not available
			ISIF=3	

General main MD INCAR tags:

IBRION=0: MD calculations are enabled by setting the IBRION tag to 0.

MDALGO specifies the molecular-dynamics-simulation protocol. *Default MDALGO=0: Standard molecular dynamics*

SMASS controls the velocities during an ab-initio molecular-dynamics run.

POTIM: sets the time step in fs for the MD run **<u>0.4</u>**

total simulation time = POTIM * NSW (fs)

NSW: sets the number of ionic steps performed. **<u>5000</u>**

TEBEG: define the desired temperature which is **<u>300</u>**

INCAR-heating

```
# Type of job

IBRION=0            #standard ab-initio MD (Verlet algorithm)

# Other Parameters

SMASS=-1            #velocities are scaled each NBLOCK step to the tempera
NBLOCK=4            #number of ionic steps between kinetic energy scaling
TEBEG=300
TEEND=300
ISIF=2              #calculate stress tensor; no change cell shape or volu
LWAVE = .FALSE.
LCHARG = .FALSE.


# Electronic relaxation
ISMEAR= 0           #partial occupencies of wavefunction have Gaussian sme
SIGMA=.35
ISYM = 0
PREC=Low

# Ionic relaxation

NSW=300

POTIM=.5
EDIFFG=-0.0001
```

TIPs:

Decreasing POTIM and increasing NSW will lead to a higher resolution result.

Use larger simulation cell to reduce the fluctuation

SMASS=-1
T=TEBEG+(TEEND-TEBEG)×NSTEP/NSW,

where NSTEP is the current step

NERSC submission script

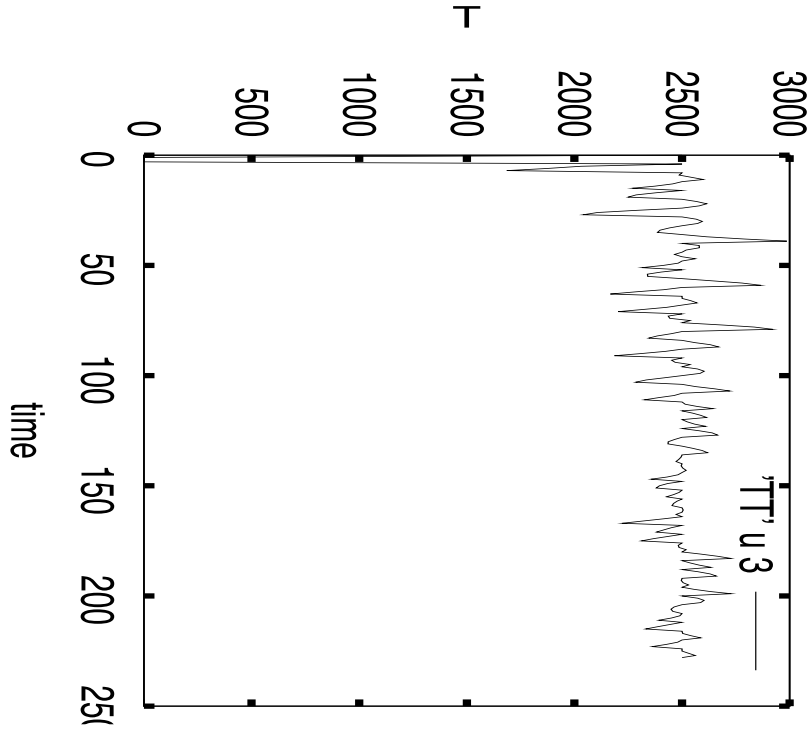
```
#!/bin/bash -l

#SBATCH -p debug
#SBATCH -N 1
#SBATCH -t 00:30:00
#SBATCH -J Ti408
#SBATCH -C knl

module load vasp #check vasp excecutable

srun -n 64 vasp_gam #check resources
```

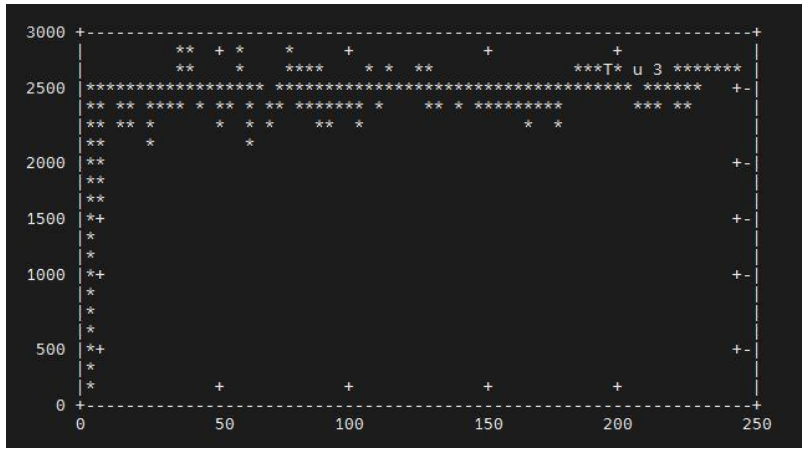
regular

= 64*N = 64*1

Monitoring temperature

- grep “T=” OSZICAR >> TT
- gnuplot > plot ‘TT’ u 3 w l





INCAR-md

```
# Type of Job

IBRION=0          #standard ab-initio MD (Verlet algorithm)
SMASS=-3          #micro canonical ensemble; total free energy conserved

# Other parameters

TEBEG=300         #note that for MD this is an ELECTRONIC temperature
                  # this sounds strange, but it does determine the
                  #change of occupation numbers f_i
                  # near the fermi energy
                  # for big electronic temperature
                  # occupation of HOMO is less than 2, say 1.5555
                  # occupation of LUMO is bigger than 0, say .44444
                  #
                  # as an experiment we can try to remove these lines from the INCAR and
                  #inspect the consequences
                  #
                  # the actual IONIC temperature is determined by momenta of
                  #each ion and is stored at the end of the CONTCAR file
                  # THIS is the reason for us to copypaste CONTCAR into POSCAR
TEEND=300
ISIF=2            #calculate stress tensor; no change cell shape or volume
LWAVE = .FALSE.
LCHARG = .FALSE.


# Electronic Relaxation

PREC=Low
ISMEAR= 0         #partial occupencies of wavefunction have Gaussian smearing
ISYM = 0          #symmetry not considered in calculation

# Ionic Relaxation

POTIM=1
NSW=1000
EDIFFG=-0.0001
```

Copy POTCAR, KPOINTS, CONTCAR from HEAT Job

Rename CONTCAR to POSCAR

Copy INCAR template for MD

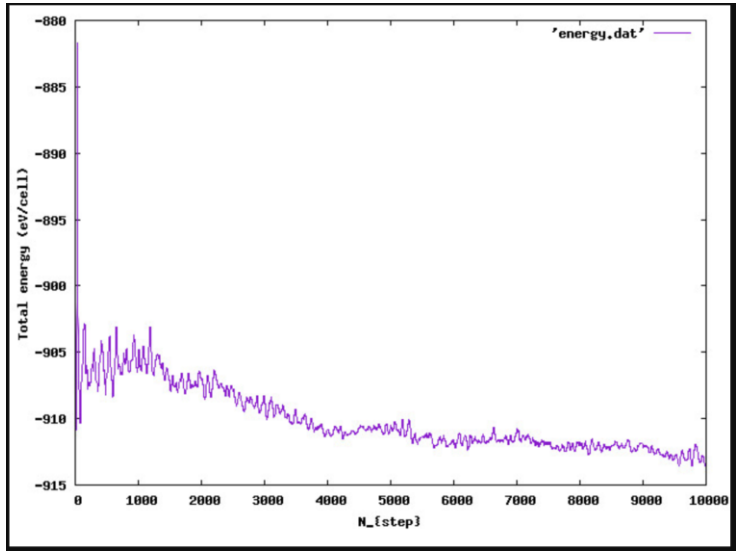
TIP:

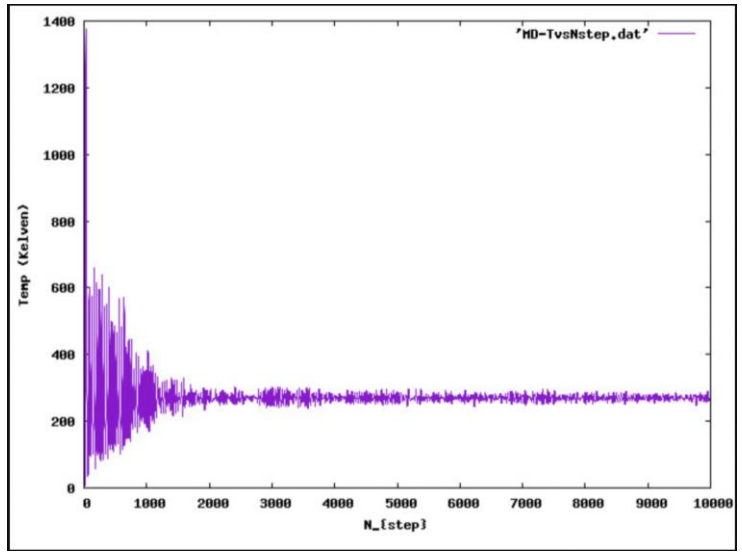
Set POTIM ≤ 0.2 for sable structure and accurate bond breaking and formation if any

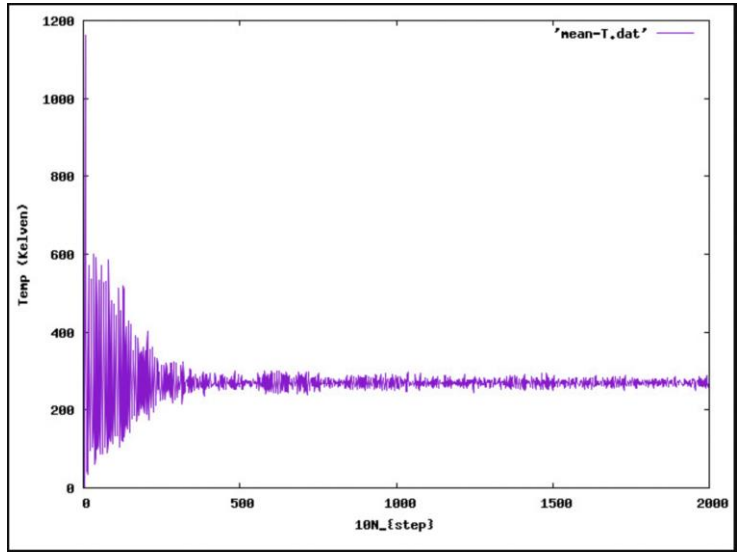
SMASS=-3 a micro canonical ensemble (NVE ensemble)

Monitoring temperature & energy

- grep "free energy" OUTCAR|awk ' {print $5}' > energy.dat
- grep "T=" OSZICAR|awk '{print $3}' > MD-TvsNstep.dat
- grep "Nose" OUTCAR|awk '{print $12}' > mean-T.dat
- gnuplot > plot ‘file-name’ u 3 w l



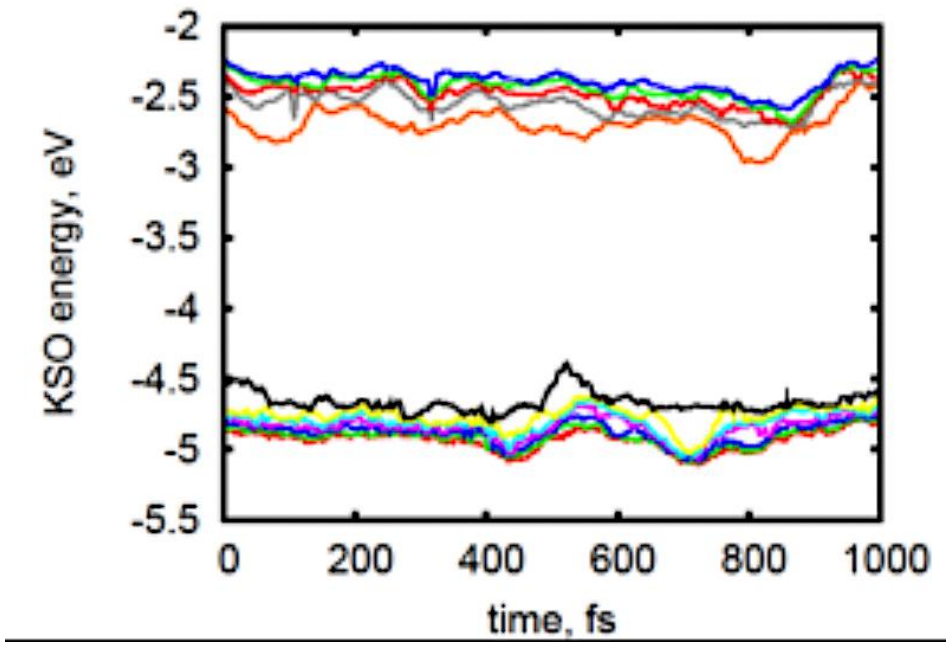




Bands Energy Fluctuation

- perl ~/bin/state_energy_extractor.pl [number of orbitals below HO] [number of orbitals above LU]

- output energy_by_band is generated
- Gnuplot ~/bin/gnuprog_fluctuations



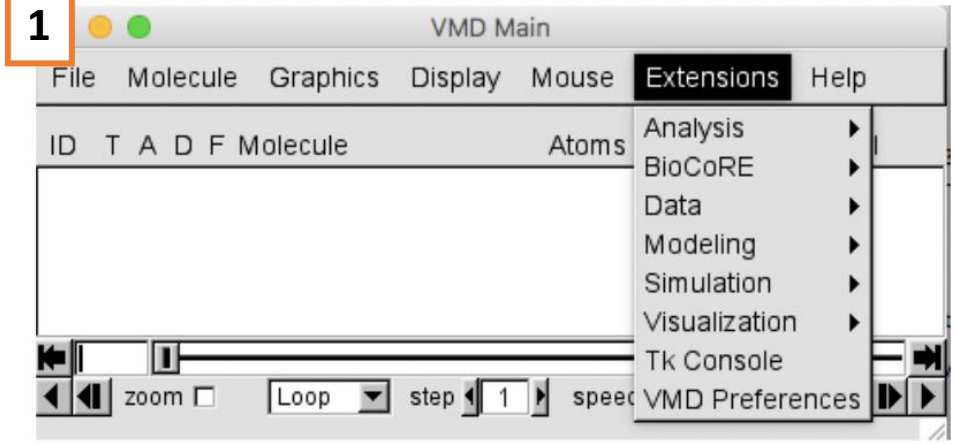
Making Movies of MD Trajectory

On the server:

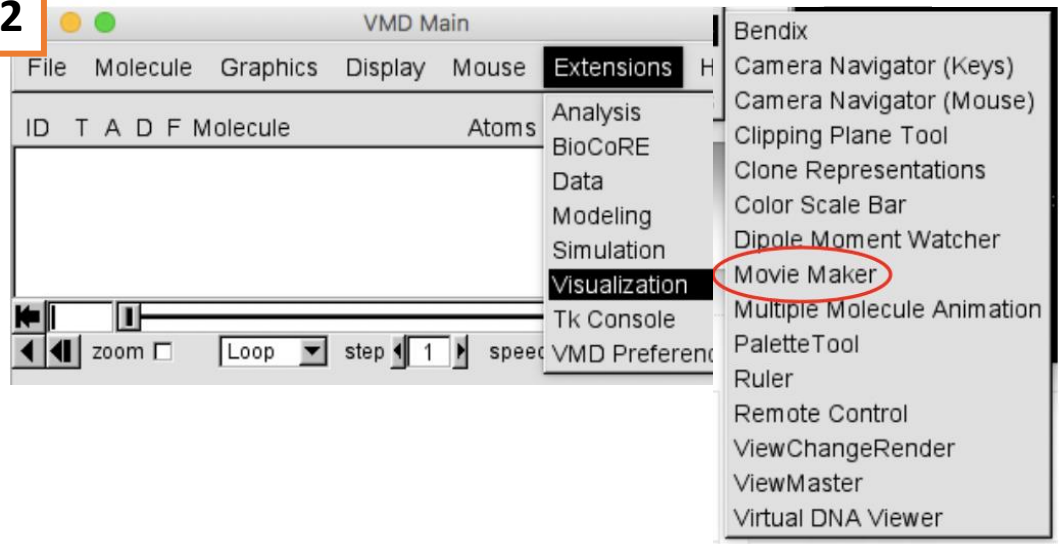
- cp ~/vtstools3/xdat2xyz.pl .
- **xdat2xyz.pl**
- ~/JMOL8/jmol.sh movie.xyz &

Making Movies of MD Trajectory

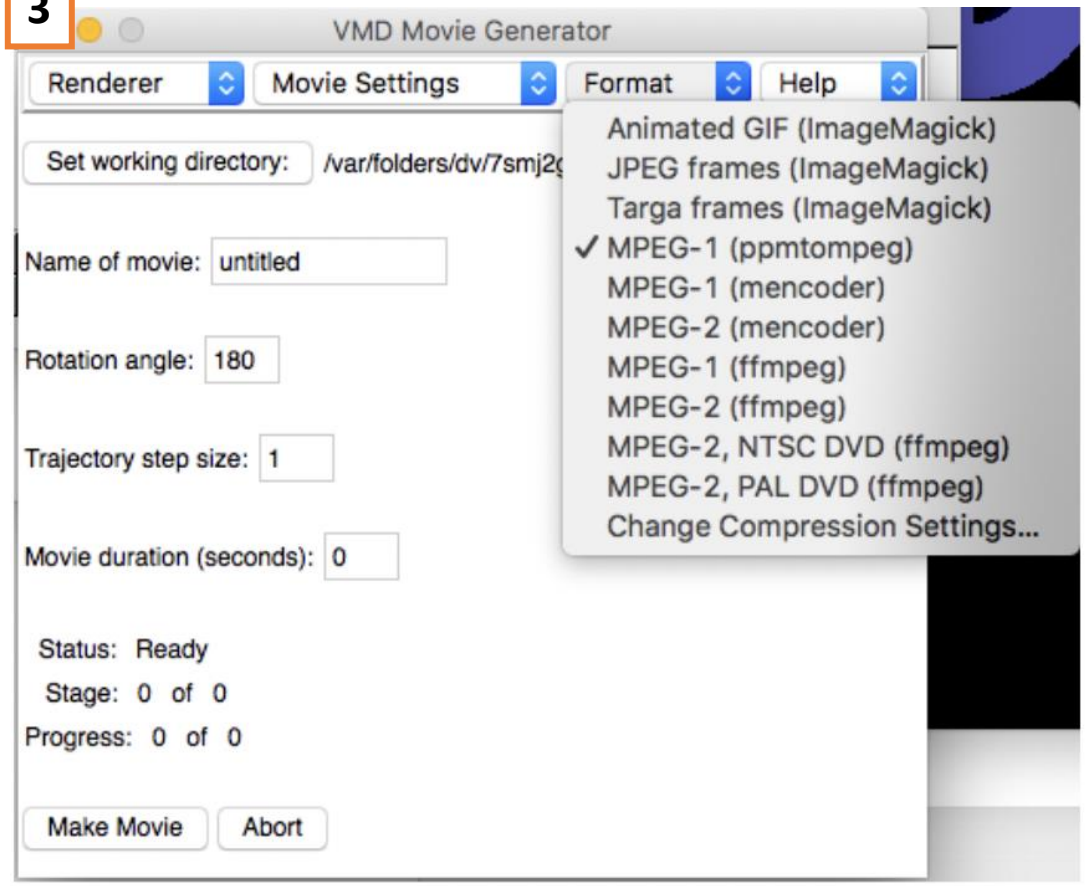
1



2



3



Thank you!

Extracting Position Snapshots from MD Trajectories

June 7, 2022

Adam Flesche

General Procedure

Optimize Geometry

Heat System

Molecular Dynamics

Extract Position Snapshots

Calculate NA coupling

Why do we need “snapshots”?

- End goal is to find NA coupling, which is found using:

$$V_{ij}(t)=\frac{1}{\Delta t}\int d\vec{r}\ \varphi_i^{KS*}(\{\vec{R}_I(t)\},\vec{r})\ \varphi_j^{KS}(\{\vec{R}_I(t+\Delta t)\},\vec{r})$$

- Knowing ionic position $\vec{R}_I$ at each timestep Δt allows us to solve the above with the help of bscript.

- Ionic positions at each timestep are extracted, giving smaller POSCAR-format files p000, p001, p002 … etc.

Special thanks to Landon for the shown equation and a very helpful explanation!

Formatting POSCAR from VASP5 to VASP4

- Make sure you have your MD trajectory job completed, enter its directory.
- First make a new directory for your snapshots so we don't make a mess, and copy everything from your MD directory to snapshots.
- Edit the POSCAR in snapshots, remove the 6th line of the file completely, and save.
- Now you are ready to grab positions!

```
C H N Zn
   1.00000000000000
    50.0610999999999962    0.0000000000000000    0.0000000000000000
     0.0000000000000000   26.0773700000000019    0.0000000000000000
     0.0000000000000000    0.0000000000000000   26.1404199999999989
   C    H    N    Zn
  114   124    8    1
Selective dynamics
Direct
  0.6057674739380254  0.5707116855134748  0.7161917631649307   T   T   T
  0.6049729272247926  0.5230921904095003  0.7957288323569973   T   T   T
  0.6112891436236891  0.6603528215211760  0.7960812534484271   T   T   T
  0.6194875381483590  0.5510590236912835  0.7589880842750089   T   T   T
  0.6345401968049980  0.4442146877999683  0.7243851923126420   T   T   T
  0.6407935419065443  0.6566019371992120  0.7873516940051689   T   T   T
  0.6486058263307962  0.5603454834306398  0.7652569974436011   T   T   T
  0.6470976794516674  0.7828459140894721  0.7508014614528263   T   T   T
  0.6566214888256779  0.6111443714361677  0.7764348029958701   T   T   T
  0.6520013738394295  0.7527482575938519  0.8005358390037188   T   T   T
  0.6602654314286337  0.4657044140557763  0.7443502857484393   T   T   T
  0.6584796658476774  0.6975803797116581  0.7908632155054002   T   T   T
  0.6668279975275966  0.5189409821456120  0.7591860107065087   T   T   T
  0.6836780753015158  0.4384794011716488  0.7496266147700128   T   T   T
```

```
C H N Zn
   1.00000000000000
    50.0610999999999962    0.0000000000000000    0.0000000000000000
     0.0000000000000000   26.0773700000000019    0.0000000000000000
     0.0000000000000000    0.0000000000000000   26.1404199999999989
   114   124    8    1
Selective dynamics
Direct
  0.6057674739380254  0.5707116855134748  0.7161917631649307   T   T   T
  0.6049729272247926  0.5230921904095003  0.7957288323569973   T   T   T
  0.6112891436236891  0.6603528215211760  0.7960812534484271   T   T   T
  0.6194875381483590  0.5510590236912835  0.7589880842750089   T   T   T
  0.6345401968049980  0.4442146877999683  0.7243851923126420   T   T   T
  0.6407935419065443  0.6566019371992120  0.7873516940051689   T   T   T
  0.6486058263307962  0.5603454834306398  0.7652569974436011   T   T   T
  0.6470976794516674  0.7828459140894721  0.7508014614528263   T   T   T
  0.6566214888256779  0.6111443714361677  0.7764348029958701   T   T   T
  0.6520013738394295  0.7527482575938519  0.8005358390037188   T   T   T
  0.6602654314286337  0.4657044140557763  0.7443502857484393   T   T   T
  0.6584796658476774  0.6975803797116581  0.7908632155054002   T   T   T
  0.6668279975275966  0.5189409821456120  0.7591860107065087   T   T   T
  0.6836780753015158  0.4384794011716488  0.7496266147700128   T   T   T
```

```
kilin@cori05:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/adam/PROJECT/FERWE_GROUND/GROUND_OPT/HEAT310K/testMD310K> ls
CHG     CONTCAR  EIGENVAL  INCAR       KPOINTS  OUTCAR  POSCAR  REPORT   XDATCAR   slurm-59751072.out  slurm-59890378.out
CHGCAR  DOSCAR   IBZKPT   INCAR-heat  OSZICAR  PCDAT   POTCAR  WAVECAR  debug.sh  slurm-59890333.out  vasprun.xml
kilin@cori05:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/adam/PROJECT/FERWE_GROUND/GROUND_OPT/HEAT310K/testMD310K> mkdir snapshots310K
kilin@cori05:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/adam/PROJECT/FERWE_GROUND/GROUND_OPT/HEAT310K/testMD310K> cd snapshots310K/
kilin@cori05:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/adam/PROJECT/FERWE_GROUND/GROUND_OPT/HEAT310K/testMD310K/snapshots310K> cp ../* .
cp: -r not specified; omitting directory '../snapshots310K'
kilin@cori05:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/adam/PROJECT/FERWE_GROUND/GROUND_OPT/HEAT310K/testMD310K/snapshots310K> vi POSCAR
kilin@cori05:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/adam/PROJECT/FERWE_GROUND/GROUND_OPT/HEAT310K/testMD310K/snapshots310K>
```

Grabbing Positions from POSCAR

- Make sure there are no other files that start with “p” in your snapshot directory: > *rm p**
- Run script: > *~/bin/outcar2poscar.pl*
- After it finishes running, you can see the individually generated POSCAR files with: > *ls p**
- These can now be used in finding NA coupling!

```
pshots310K> ls p*
p000  p062   p1021  p1078  p140  p202  p264  p326  p388  p450  p512  p574  p636  p698  p760  p822  p884  p946
p001  p063   p1022  p1079  p141  p203  p265  p327  p389  p451  p513  p575  p637  p699  p761  p823  p885  p947
p002  p064   p1023  p108   p142  p204  p266  p328  p390  p452  p514  p576  p638  p700  p762  p824  p886  p948
p003  p065   p1024  p1080  p143  p205  p267  p329  p391  p453  p515  p577  p639  p701  p763  p825  p887  p949
p004  p066   p1025  p1081  p144  p206  p268  p330  p392  p454  p516  p578  p640  p702  p764  p826  p888  p950
p005  p067   p1026  p1082  p145  p207  p269  p331  p393  p455  p517  p579  p641  p703  p765  p827  p889  p951
p006  p068   p1027  p1083  p146  p208  p270  p332  p394  p456  p518  p580  p642  p704  p766  p828  p890  p952
p007  p069   p1028  p1084  p147  p209  p271  p333  p395  p457  p519  p581  p643  p705  p767  p829  p891  p953
p008  p070   p1029  p1085  p148  p210  p272  p334  p396  p458  p520  p582  p644  p706  p768  p830  p892  p954
p009  p071   p103   p1086  p149  p211  p273  p335  p397  p459  p521  p583  p645  p707  p769  p831  p893  p955
p010  p072   p1030  p1087  p150  p212  p274  p336  p398  p460  p522  p584  p646  p708  p770  p832  p894  p956
p011  p073   p1031  p1088  p151  p213  p275  p337  p399  p461  p523  p585  p647  p709  p771  p833  p895  p957
p012  p074   p1032  p1089  p152  p214  p276  p338  p400  p462  p524  p586  p648  p710  p772  p834  p896  p958
p013  p075   p1033  p109   p153  p215  p277  p339  p401  p463  p525  p587  p649  p711  p773  p835  p897  p959
p014  p076   p1034  p1090  p154  p216  p278  p340  p402  p464  p526  p588  p650  p712  p774  p836  p898  p960
p015  p077   p1035  p1091  p155  p217  p279  p341  p403  p465  p527  p589  p651  p713  p775  p837  p899  p961
p016  p078   p1036  p1092  p156  p218  p280  p342  p404  p466  p528  p590  p652  p714  p776  p838  p900  p962
p017  p079   p1037  p1093  p157  p219  p281  p343  p405  p467  p529  p591  p653  p715  p777  p839  p901  p963
p018  p080   p1038  p1094  p158  p220  p282  p344  p406  p468  p530  p592  p654  p716  p778  p840  p902  p964
p019  p081   p1039  p1095  p159  p221  p283  p345  p407  p469  p531  p593  p655  p717  p779  p841  p903  p965
p020  p082   p104   p1096  p160  p222  p284  p346  p408  p470  p532  p594  p656  p718  p780  p842  p904  p966
p021  p083   p1040  p1097  p161  p223  p285  p347  p409  p471  p533  p595  p657  p719  p781  p843  p905  p967
p022  p084   p1041  p1098  p162  p224  p286  p348  p410  p472  p534  p596  p658  p720  p782  p844  p906  p968
p023  p085   p1042  p1099  p163  p225  p287  p349  p411  p473  p535  p597  p659  p721  p783  p845  p907  p969
p024  p086   p1043  p110   p164  p226  p288  p350  p412  p474  p536  p598  p660  p722  p784  p846  p908  p970
p025  p087   p1044  p1100  p165  p227  p289  p351  p413  p475  p537  p599  p661  p723  p785  p847  p909  p971
p026  p088   p1045  p1101  p166  p228  p290  p352  p414  p476  p538  p600  p662  p724  p786  p848  p910  p972
p027  p089   p1046  p1102  p167  p229  p291  p353  p415  p477  p539  p601  p663  p725  p787  p849  p911  p973
p028  p090   p1047  p1103  p168  p230  p292  p354  p416  p478  p540  p602  p664  p726  p788  p850  p912  p974
p029  p091   p1048  p1104  p169  p231  p293  p355  p417  p479  p541  p603  p665  p727  p789  p851  p913  p975
p030  p092   p1049  p1105  p170  p232  p294  p356  p418  p480  p542  p604  p666  p728  p790  p852  p914  p976
p031  p093   p105   p1106  p171  p233  p295  p357  p419  p481  p543  p605  p667  p729  p791  p853  p915  p977
p032  p094   p1050  p1107  p172  p234  p296  p358  p420  p482  p544  p606  p668  p730  p792  p854  p916  p978
p033  p095   p1051  p111   p173  p235  p297  p359  p421  p483  p545  p607  p669  p731  p793  p855  p917  p979
p034  p096   p1052  p112   p174  p236  p298  p360  p422  p484  p546  p608  p670  p732  p794  p856  p918  p980
p035  p097   p1053  p113   p175  p237  p299  p361  p423  p485  p547  p609  p671  p733  p795  p857  p919  p981
p036  p098   p1054  p114   p176  p238  p300  p362  p424  p486  p548  p610  p672  p734  p796  p858  p920  p982
p037  p099   p1055  p115   p177  p239  p301  p363  p425  p487  p549  p611  p673  p735  p797  p859  p921  p983
p038  p100   p1056  p116   p178  p240  p302  p364  p426  p488  p550  p612  p674  p736  p798  p860  p922  p984
p039  p1000  p1057  p117   p179  p241  p303  p365  p427  p489  p551  p613  p675  p737  p799  p861  p923  p985
p040  p1001  p1058  p118   p180  p242  p304  p366  p428  p490  p552  p614  p676  p738  p800  p862  p924  p986
p041  p1002  p1059  p119   p181  p243  p305  p367  p429  p491  p553  p615  p677  p739  p801  p863  p925  p987
p042  p1003  p106   p120   p182  p244  p306  p368  p430  p492  p554  p616  p678  p740  p802  p864  p926  p988
p043  p1004  p1060  p121   p183  p245  p307  p369  p431  p493  p555  p617  p679  p741  p803  p865  p927  p989
p044  p1005  p1061  p122   p184  p246  p308  p370  p432  p494  p556  p618  p680  p742  p804  p866  p928  p990
p045  p1006  p1062  p123   p185  p247  p309  p371  p433  p495  p557  p619  p681  p743  p805  p867  p929  p991
p046  p1007  p1063  p124   p186  p248  p310  p372  p434  p496  p558  p620  p682  p744  p806  p868  p930  p992
p047  p1008  p1064  p125   p187  p249  p311  p373  p435  p497  p559  p621  p683  p745  p807  p869  p931  p993
p048  p1009  p1065  p126   p188  p250  p312  p374  p436  p498  p560  p622  p684  p746  p808  p870  p932  p994
p049  p101   p1066  p127   p189  p251  p313  p375  p437  p499  p561  p623  p685  p747  p809  p871  p933  p995
p050  p1010  p1067  p128   p190  p252  p314  p376  p438  p500  p562  p624  p686  p748  p810  p872  p934  p996
p051  p1011  p1068  p129   p191  p253  p315  p377  p439  p501  p563  p625  p687  p749  p811  p873  p935  p997
p052  p1012  p1069  p130   p192  p254  p316  p378  p440  p502  p564  p626  p688  p750  p812  p874  p936  p998
p053  p1013  p107   p131   p193  p255  p317  p379  p441  p503  p565  p627  p689  p751  p813  p875  p937  p999
p054  p1014  p1070  p132   p194  p256  p318  p380  p442  p504  p566  p628  p690  p752  p814  p876  p938
p055  p1015  p1071  p133   p195  p257  p319  p381  p443  p505  p567  p629  p691  p753  p815  p877  p939
p056  p1016  p1072  p134   p196  p258  p320  p382  p444  p506  p568  p630  p692  p754  p816  p878  p940
p057  p1017  p1073  p135   p197  p259  p321  p383  p445  p507  p569  p631  p693  p755  p817  p879  p941
```

Next steps: finding WAVECAR at each timestep and extract NA couplings using bscript!

Questions?

Setting Up bscript to Create Multiple Launches From One Script

Adapted for the Example of Creating Nonadiabatic Coupling Without Spin Data Based on Molecular Dynamic Trajectory Data

Hadassah B. Griffin

Computational Chemistry Skills Summer 2022

Overview

All programs executed in NERSC

```
_2/nonadiabaticNoSpinCoupling> more cori-coupling.sh
#!/bin/bash -l

#SBATCH -q debug
#SBATCH -N 1
#SBATCH -t 00:15:00
#SBATCH -L SCRATCH
#SBATCH -J coupl
#SBATCH -C knl

#module load PrgEnv-gnu/6.0.5
module load vasp/5.4.4-knl #check vasp excutable

./bscipt.sh #generate couplings
```

```
_2/nonadiabaticNoSpinCoupling> more bscipt.sh
module swap PrgEnv-intel PrgEnv-gnu
mv p99 POSCAR
srun -n 64 vasp_std
./extract_energy_pop.exe
./osc_str.exe
rm energy_pop
for((i=100;$i<=105;i=$(($i+1))));
do
j=$(printf "%.3d" "$i")
echo p$j
cp WAVECAR WAVECAROLD
mv p$j POSCAR
srun -n 64 vasp_std
./extract_energy_pop.exe
./osc_str_overlap.exe
mv OS_STRENGTH os.$j
mv forMasterEq forMasterEq.$j
gzip forMasterEq.$j
mv coupling coupling.$j
gzip coupling.$j
gzip OS_STRENGTH os.$j
mv billdata billdata.$j
gzip billdata.$j
rm energy_pop
done
```

Nonadiabatic Spin Coupling: Completed Calculations Required

- Assumed calculations completed and files ready:
  - Molecular dynamic (MD) trajectory has been calculated
    - WAVECAR
    - XDATCAR
    - POSCAR (Needs to be in VASP 4 Format)
    - POTCAR (*very important to have, especially if you choose do this work in a different directory*)
  - Oscillator Strength Calculations
    - input_overlap
    - energy_pop
      - Use "perl ~/bin/state_energy_extractor.pl" to create

Doing the VASP 4 POSCAR Modification

- VASP 5

```
_2/nonadiabaticNoSpinCoupling> head ../nvt_thermostat/POSCAR
CD Pb Se
   1.00000000000000
    17.2883522845873010    0.0000000000000000    0.0000000000000000
     0.0000000000000000   18.6227501583016100    0.0000000000000000
     0.0000000000000000    0.0000000000000000   27.9510180275233502
   Cd   Pb   Se
Selective dynamics
Direct
  0.4545916843363247  0.1993545839935950  0.2439944378655387   T   T   T
```

- VASP 4

```
_2/nonadiabaticNoSpinCoupling> head POSCAR
 CD Pb Se
 1.00000000000000000
    17.2883522845873010    0.0000000000000000    0.0000000000000000
     0.0000000000000000   18.6227501583016100    0.0000000000000000
     0.0000000000000000    0.0000000000000000   27.9510180275233502
 33 16 49
Selective dynamics
Direct
  0.4675517867140083  0.1820477626119422  0.2367731291033196   T T T
  0.4666957190126812  0.5773121536083853  0.1518416966359082   T T T
```

Remove this line from POSCAR to get it into VASP 4 format

-Do this BEFORE generating position snapshots

Creating the Trajectory/Position Snapshots (1)

- Multiple files available; use “perl” command to run
  - perl /global/common/cori_cle7up03/software/vasp/vtstscripts/3.1/xdat2pos.pl 0 t1 t2
    - Inputs: time stamp start, step, end
    - Outputs: POSCAR#.out
    - Note: default bscript would have to be modified for the different position file name, but I have not tested this for myself
    - Useful to see if position data extractable

Creating the Trajectory/Position Snapshots (2)

- perl ~/bin/outcar2poscar.pl (used in this presentation)
  - Outputs: p000 ~ p999 in trajectory
  - Note: POSCAR must be in VASP 4 format prior to calculation

```
kilin@cori03:/global/cfs/cdirs/m1251/vasp/CHEM676_2022/hgriffin/sum22_project/hybrid_initial_ZShift
_2/nonadiabaticNoSpinCoupling> ls p*
p000  p063  p132  p195  p258  p321  p384  p447  p510  p573  p636  p699  p762  p825  p888  p951
p001  p064  p133  p196  p259  p322  p385  p448  p511  p574  p637  p700  p763  p826  p889  p952
p002  p065  p134  p197  p260  p323  p386  p449  p512  p575  p638  p701  p764  p827  p890  p953
p003  p066  p135  p198  p261  p324  p387  p450  p513  p576  p639  p702  p765  p828  p891  p954
p004  p067  p136  p199  p262  p325  p388  p451  p514  p577  p640  p703  p766  p829  p892  p955
p005  p068  p137  p200  p263  p326  p389  p452  p515  p578  p641  p704  p767  p830  p893  p956
```

Copy Templates Relevant for Coupling Calculations

- Nonadiabatic Couplings Without Spin Files
  - Get INCAR template:
    - cp ~/bin/INCAR/INCAR_for_coupling
  - Copy these files from: "~/bin/COUPLINGS/NOSPIN/"
    - cori-coupling.sh
    - osc_str.exe
    - bscipt.sh
    - extract_energy_pop.exe
    - osc_str_overlap.exe

Modify cori-coupling.sh As Needed (Default shown below)

```
_2> more ~/bin/COUPLINGS/NOSPIN/cori-coupling.sh
#!/bin/bash -l

#SBATCH -q regular
#SBATCH -N 1
#SBATCH -t 48:00:00
#SBATCH -L SCRATCH
#SBATCH -J silll
#SBATCH -C knl

#module load PrgEnv-gnu/6.0.5
module load vasp/5.4.4-knl #check vasp excutable

./bscipt.sh #generate couplings
```

Note: optional to comment out (#) specifics of VASP executable, since it updates occasionally

Modify bsipt.sh

```
_2/nonadiabaticNoSpinCoupling> more bscipt.sh
module swap PrgEnv-intel PrgEnv-gnu
cp p105 POSCAR
srun -n 256 vasp_std
cp OUTCAR OUTCARinitial
./extract_energy_pop.exe
./osc_str.exe
rm energy_pop
for((i=106;$i<=999;i=$(($i+1))));
do
j=$(printf "%.3d" "$i")
echo p$j
cp WAVECAR WAVECAROLD
cp p$j POSCAR
srun -n 256 vasp_std
cp OUTCAR OUTCAR$j
./extract_energy_pop.exe
./osc_str_overlap.exe
mv OS_STRENGTH os.$j
mv forMasterEq forMasterEq.$j
gzip forMasterEq.$j
mv coupling coupling.$j
gzip coupling.$j
gzip OS_STRENGTH os.$j
mv billdata billdata.$j
gzip billdata.$j
rm energy_pop
done
```

Advisory: if your program encounters errors in mid-calculation, your energy_pop will be deleted before a new one is created. Have a copy elsewhere.

Change “prior position step” name

Change to range of position data. This example would look at p106 -> p999.

Output of bscipt Calculation

- After “sbatch cori-coupling.sh”…
- Intermediate calculation data files (OUTCAR###, billdata.###.gz, forMasterEq.###, etc)
- Compressed .gz Matlab files with Coupling Data
- Transfer coupling.###.gz files to personal system (not NERSC) for analysis (use WinSCP, scp command, etc.)

```
_2/nonadiabaticNoSpinCoupling> ls -lt coup*
-rw-rw---- 1 kilin m1251 32357 Jun  6 18:08 coupling.105.gz
-rw-rw---- 1 kilin m1251 32377 Jun  6 18:01 coupling.104.gz
-rw-rw---- 1 kilin m1251 32533 Jun  6 17:54 coupling.103.gz
-rw-rw---- 1 kilin m1251 32557 Jun  6 17:47 coupling.102.gz
-rw-rw---- 1 kilin m1251 32566 Jun  6 17:40 coupling.101.gz
```

Extracting .gz Data

- Use Matlab on personal computer
- If not installed, available to NDSU students. Install instructions: https://kb.ndsu.edu/page.php?id=102044
- Matlab commands to extract files: https://www.mathworks.com/help/matlab/ref/gunzip.html

.gz Data Extracted Example

coupling.100 - Notepad

File Edit Format View Help

```
 -0.0000000000000000E+00   0.1211389995124899E-03  -0.6197786083137757E-02  -0.1541268113405541E-03  -0.4665970657928903E-03  -0.7284804391835226E-06  -0
6 -0.3712556368651512E-03   0.4630682634980034E-03   0.1576053499758531E-02   0.2686240203408773E-03  -0.2817562003593859E-05   0.1069117804793182E-03
 -0.1211389995124962E-03  -0.0000000000000000E+00  -0.1942889889451166E-02  -0.2934619967660107E-04  -0.3449961594232367E-03  -0.5720943450691436E-04  -0
5  0.1409516499782699E-02  -0.1720036907262898E-02   0.3654887808048720E-03  -0.4391203553994685E-03  -0.1405275479990537E-04  -0.2636230670092730E-03  -
  0.6197786083137771E-02   0.1942889889451183E-02  -0.0000000000000000E+00  -0.7764667077451572E-02  -0.9418347748795779E-02  -0.3641769608860657E-02  -0
3  0.7172173383769450E-05   0.1588846601055998E-04  -0.7402806884876052E-04  -0.1839076744784260E-03   0.1406254361916174E-03  -0.1595769545653356E-02  -
  0.1541268113405569E-03   0.2934619967659536E-04   0.7764667077451625E-02  -0.0000000000000000E+00  -0.5442068688634970E-04  -0.7399482143182013E-05   0
5  0.8147527446915128E-04  -0.1279817206778083E-02  -0.2147470034128239E-02   0.3756503423469096E-04  -0.6351919845011192E-05   0.1170861671666793E-03
  0.4665970657928879E-03   0.3449961594232396E-03   0.9418347748795812E-02   0.5442068688635083E-04  -0.0000000000000000E+00  -0.1082556954166193E-03  -0
4  0.3155030115476390E-03   0.4742545116766383E-03  -0.3953234509227207E-03   0.6585269071154072E-03  -0.1051286563581257E-04  -0.9593368242064691E-04  -
  0.7284804391805252E-06   0.5720943450690465E-04   0.3641769608860670E-02   0.7399482143181728E-05   0.1082556954166220E-03  -0.0000000000000000E+00   0
5 -0.7789382572264318E-04  -0.4918035795713477E-04   0.8358939398922751E-03   0.4946173463725304E-03   0.1789697471617917E-04   0.5764820143031575E-04
  0.1140873991442991E-02   0.1432305801718290E-02   0.1172223214949838E-02  -0.1836694093142026E-04   0.4625082604997933E-02  -0.3203474393597199E-02  -0
3 -0.4937913311601177E-03  -0.2047925846833034E-03   0.4841258794915996E-04   0.2448004520155315E-04   0.9538028161483181E-03  -0.8179970757129417E-03  -
 -0.7351337966062313E-03   0.2755885778417386E-02   0.2010363014286351E-04   0.8302554893948310E-02  -0.7796306674612566E-03   0.5018208250160646E-02  -0
3  0.4066768918310286E-04   0.4983203543263708E-04   0.1427379850213297E-05  -0.1338241433340649E-03  -0.6432566532606143E-03   0.9390104445749310E-04
  0.3464381375877070E-02   0.2094393903502979E-02  -0.2674171380057323E-04  -0.1866487823164306E-02  -0.2774545831173212E-02  -0.3707383767785820E-02   0
4 -0.9287501015799861E-05  -0.1808451408814952E-04   0.4249251971306221E-05  -0.2164251603272381E-03   0.4082972067911226E-03  -0.1623765903295071E-03  -
  0.5884735406687424E-04   0.2009563250585614E-04  -0.4568929786453768E-03   0.3119493542676671E-04   0.1636378276699923E-03   0.1413856780440620E-03  -0
5 -0.4154947995917303E-03  -0.1583683773587770E-02   0.1516073602411404E-03   0.6382657444088657E-03   0.4552270039605295E-04   0.1408083718593092E-03  -
  0.2318038117841902E-04  -0.3032236516115918E-04  -0.5381126147706148E-03   0.1111079409617846E-04  -0.5225615371857403E-03  -0.3639274561958678E-03  -0
5 -0.4989412914218860E-04  -0.4056034644302328E-03  -0.1236727195024489E-02   0.1210981091431362E-03  -0.8071653559951480E-04  -0.1626318185846360E-03
  0.1238029790038439E-02  -0.1356933237974979E-02  -0.2880162650038234E-05  -0.3096782893248831E-02   0.1923980010761557E-03   0.6348920088952949E-03  -0
3 -0.2509575199191379E-03  -0.2937270255068735E-04   0.5721382245375038E-04   0.1067661794551621E-03   0.1737717791179464E-02   0.5425940852857329E-03
  0.1163297737875148E-02  -0.9187530084712909E-03   0.2730810398346340E-03  -0.4850194504941107E-02  -0.6021359794605949E-03  -0.1044154753788815E-02  -0
3 -0.6757781068721203E-05   0.5815755118486926E-04   0.9004034695129296E-05  -0.1375061256461829E-03   0.2186777254697165E-03  -0.7236096313513609E-03
 -0.2648088907195762E-02  -0.2503624521019339E-02   0.7340779284267858E-05  -0.4648582726231577E-02   0.5671677647293649E-03   0.2729668397321536E-02  -0
2  0.1038408478510598E-04  -0.2635984465563676E-04   0.4138622204178861E-05  -0.5339659776272278E-03   0.1212472194892008E-02   0.1730199635224596E-02
 -0.1209882437876063E-02   0.4800088231299373E-03  -0.2225445365786877E-03   0.5146088155954648E-02  -0.2544218777471719E-03   0.2506098258927214E-02   0
```

Ln 1, Col 1 | 100% | Unix (LF) | UTF-8

Setting Up The bscript

Equations: Why We Need To Keep Recomputing The WAVECAR

What’s In The WAVECAR File?

A bunch of binary data that you’ll have to read through Fortran scripts

```
NBAND        number of bands
ENCUTI       'initial' cut-off energy
AX           'initial' basis vectors defining the supercell
CELEN        ('initial') eigenvalues
FERWE        ('initial') Fermi-weights
CPTWFP       ('initial') wavefunctions
```

https://www.vasp.at/wiki/index.php/WAVECAR

I highly recommend the VASP wiki as a resource for these kinds of questions:
https://www.vasp.at/wiki/index.php/The_VASP_Manual

Why Do We Care?

We need the wavefunctions!

In equilibrium geometry (which is what DFT converges to),
the wavefunctions (or KS orbitals in this case) are orthogonal.

That means that there's no "overlap" between our orbitals.

And that means that there's no way for the electrons to transition from one orbital to another.

How Do We Get Around This Problem?

We use nuclear motion (molecular dynamics) to our advantage!

If we look at two neighboring “snapshots” of our nuclear configurations (e.g. p134 and p135), the nuclei will be in slightly different positions.

This means that the sets of orbitals will also be slightly different.

And that means that the orbitals from our first snapshot won’t be orthogonal to the orbitals from our second snapshot!

How Do We Use This?

We have supercomputers do disgusting integrals so we don't have to!

Imagine we only shift the position of the Ith nucleus by a little bit. Then the "overlap" of the orbitals between our snapshots will be given by

$$V_{ij}(\Delta\vec{R}_I) = \frac{1}{\Delta R_I}\int d\vec{r}\,\varphi_i^*(\vec{r},\vec{R}_1,\dots,\vec{R}_I,\dots,\vec{R}_N)\,\varphi_j(\vec{r},\vec{R}_1,\dots,\underbrace{\vec{R}_I+\Delta\vec{R}_I}_{\text{Slightly shifted nucleus}},\dots,\vec{R}_N) \neq \delta_{ij}$$

i^{th} wavefunction from our first snapshot

j^{th} wavefunction from our second snapshot

Kronecker delta

Johnson, L.; Kilin, D., Effect of ligand groups on photoexcited charge carrier dynamics at the perovskite/TiO2 interface. *Rsc Advances* **2021,** *12* (1), 78-87.

What About The Real Equation?

In our systems, all of the nuclei might have moved. Then we have

$$V_{ij}(t) = -\frac{i\hbar}{\Delta t}\int d\vec{r}\,\varphi_i^*\left(\vec{r},\underbrace{\{\vec{R}_I(t)\}}_{\text{Set of nuclear positions from our first snapshot}}\right)\varphi_j\left(\vec{r},\underbrace{\{\vec{R}_I(t+\Delta t)\}}_{\text{Set of nuclear positions from our second snapshot}}\right)$$

This is the equation that we actually use.

Johnson, L.; Kilin, D., Effect of ligand groups on photoexcited charge carrier dynamics at the perovskite/TiO2 interface. *Rsc Advances* **2021,** *12* (1), 78-87.

What Do We Do With The Overlaps?

Electron dynamics! I used Redfield Theory. Redfield, A. G., The Theory of Relaxation Processes**This work was started while the author was at Harvard University, and was then partially supported by Joint Services Contract N5ori-76, Project Order I. In *Advances in Magnetic and Optical Resonance*, Waugh, J. S., Ed. Academic Press: 1965; Vol. 1, pp 1-32.

The Redfield tensor

V is in there somewhere

$$R_{ijkl} = \Gamma^{+}_{ijkl} + \Gamma^{-}_{ijkl} - \delta_{ij} \sum_{m} \Gamma^{+}_{kmml} - \delta_{kl} \sum_{m} \Gamma^{-}_{immj}$$

is used to solve the time-dependent electron density matrix

$$\frac{d\rho_{ij}}{dt} = \frac{-i}{h} \sum_{k} (F_{ik}\rho_{kj} - \rho_{ik}F_{kj}) + \left(\frac{d\rho_{ij}}{dt}\right)_{diss}$$

which gives us electronic transition rates!

R is in there somewhere

Johnson, L.; Kilin, D., Effect of ligand groups on photoexcited charge carrier dynamics at the perovskite/TiO2 interface. *Rsc Advances* **2021,** *12* (1), 78-87.

Enter The bscript:

bash script

~/bin/bscript_spin_YH.sh

note that there are several versions of the bscript and I haven't done any verifications on them recently. You'll want a different version depending on how you're handling spin and such

Loop through all of our snapshots

Save a copy of our "first" snapshot, so it doesn't get overwritten

Update the nuclear positions

Run VASP

These scripts pulls data from WAVECAR,
you may need to change the exact script/directory

The coupling files contain the values of V_{ij} for all the pairs of orbitals i and j of interest.

Format it to e.g. p005 instead of p5

Might have to change this

```
module swap PrgEnv-intel PrgEnv-gnu
mkdir UP
mkdir DOWN

cp p000 POSCAR
srun -n64 -c4 --cpu-bind=cores vasp_gam
~/bin/SPIN_OS/extract_energy_pop
cp energy_pop UP/energy_pop_up.000
cp energy_pop_down DOWN/energy_pop_down.000

for((i=1;$i<1000;i=$(($i+1)))); do
        j=$(printf "%.3d" "$i")
        echo p$j

        cp WAVECAR WAVECAROLD
        cp p$j POSCAR
        srun -n64 -c4 --cpu-bind=cores vasp_gam

        ~/bin/SPIN_OS/extract_energy_pop
        cp energy_pop UP/energy_pop_up.$j
        cp energy_pop_down DOWN/energy_pop_down.$j

        ~/bin/SPIN_OS/OS_dipol_spin_up_t
        mv OS_STRENGTH UP/os.$j
        ~/bin/SPIN_OS/ovlap_spin_polar_t
        mv OS_STRENGTH os.$j
        mv forMasterEq forMasterEq.$j
        gzip forMasterEq.$j
        mv coupling coupling.$j
        gzip coupling.$j
        gzip OS_STRENGTH os.$j
        mv coupling* UP/.
        mv OS_STR* UP/.
        mv os* UP/.
        rm billdata

        ~/bin/SPIN_OS/OS_dipol_spin_down_t
        mv OS_STRENGTH DOWN/os.$j
        ~/bin/SPIN_OS/ovlap_spin_polar_down_t
        mv OS_STRENGTH os.$j
        mv forMasterEq forMasterEq.$j
        gzip forMasterEq.$j
        mv coupling coupling.$j
        gzip coupling.$j
        gzip OS_STRENGTH os.$j
        mv coupling* DOWN/.
        mv OS_STR* DOWN/.
        mv os* DOWN/.
        rm billdata

        rm energy_pop

done
```

Calculation of V_{ij}

~/bin/K-OS/overlap.f

Fortran script

Many bscripts will directly call an overlap.f script

This is the definition of the NAC function that calculates non-adiabatic couplings (V_{ij}), found at line 1033

”T” generally means “first snapshot” and “dT” generally means “second snapshot”

These are for multiline commands

```
      subroutine NAC(WT,WdT,NtdtKt,Nt,Ntdt,DD,nbandmin,nbandmax,
     & ikw,ikw1,nwk,npdim,nbdim,nwdim,nsdim,nSize,ispin,npw)
      implicit real*8 (a-h,o-z)
      complex*8 WT(npdim,nbdim,nwdim,nsdim),
     & WdT(npdim,nbdim,nwdim,nsdim)
      real*8 NtKtdt(nbandmin:nbandmax,nbandmin:nbandmax),
     & Nt(nbandmin:nbandmax),Ntdt(nbandmin:nbandmax),
     & DD(nbandmin:nbandmax,nbandmin:nbandmax),
     & NORM1,NORM2,NtdtKt
      CHARACTER(LEN=20) :: t1,t2,t3
      CHARACTER (LEN=16)      :: fileout ! file name for output
      write(fileout,'(A9,I2.2,A1,I2.2,A1,I1.1)') 'coupling.',ikw,'.',
     & ikw1,'.',ispin
c       write(fileout,'(A8)') 'coupling'
      POTIM=1D0
      open(141,file=fileout)
      do i=1,nSize
        Nt(i)=0D0
        Ntdt(i)=0D0
        do j=1,nSize
          NtKtdt(i,j)=0D0
          DD(i,j)=0D0
        enddo
      enddo
```

comment

comment

Calculation of V_{ij}

~/bin/K-OS/overlap.f

Fortra

Many bscripts will directly call an overlap

This is the definition of the NAC function
calculates non-adiabatic couplings (V_{ij}),
line 1033

”T” generally means “first snapshot” and
generally means “second snapshot”

```
     & Wdf(npdim,nbdim,nwdim,nsdim)
       real*8 NtKtdt(nbandmin:nbandmax,nbandmin:nbandmax),
     & Nt(nbandmin:nbandmax),Ntdt(nbandmin:nbandmax),
     & DD(nbandmin:nbandmax,nbandmin:nbandmax),
     & NORM1,NORM2,NtdtKt
        CHARACTER(LEN=20) :: t1,t2,t3
       CHARACTER (LEN=16)      :: fileout ! file name for output
        write(fileout,'(A9,I2.2,A1,I2.2,A1,I1.1)') 'coupling.',ikw,'.',
     & ikw1,'.',ispin
          write(fileout,'(A8)') 'coupling'
        POTIM=1D0
        open(141,file=fileout)
        do i=1,nSize
          Nt(i)=0D0
          Ntdt(i)=0D0
          do j=1,nSize
            NtKtdt(i,j)=0D0
            DD(i,j)=0D0
          enddo
        enddo
!-----------------------------------------------------------------------
! Overlap of "old wavecar" with other "old wavecar": <psi(t+dt)|psi(t+dt)>
!-----------------------------------------------------------------------
            do i=nbandmin,nbandmax
            overlap=0D0
              do k=1,npw
            overlap=overlap+WT(k,i,ikw,ispin)*
     &conjg(WT(k,i,ikw,ispin))
              enddo
             Nt(i)=overlap
        print*,'Nt(i)=',Nt(i)
            enddo
```

Calculation of V_{ij}

~/bin/K-OS/overlap.f

```
c              print*,'Ntdt(i)=',Ntdt(i),Nt(i)
            enddo
!-----------------------------------------------------------------------
! Overlap of "old wavecar" with "new wavecar": 1-st part of <psi(t+dt)|psi(t)>
!-----------------------------------------------------------------------
          do i=nbandmin,nbandmax
            do j=nbandmin,nbandmax
            overlap=0D0
              do k=1,npw
                overlap=overlap+WdT(k,j,ikw1,ispin)*
   &conjg(WT(k,i,ikw,ispin))
              enddo
               NtKtdt(i,j)=overlap
c           write(401,*) NtKtdt(i,j)
c                 print*,overlap
            enddo !j-cycle
          enddo ! i-cycle
c          print*,'cycle 1',overlap
!-----------------------------------------------------------------------
```

$$V_{ij}(t) = -\frac{i\hbar}{\Delta t}\int d\vec{r}\,\varphi_i^*\left(\vec{r},\{\vec{R}_I(t)\}\right)$$

$$\varphi_j\left(\vec{r},\{\vec{R}_I(t+\Delta t)\}\right)$$

Calcula

Many bscripts will

This is the definitio
calculates non-adia
line 1033

”T” generally mear
generally means “s

```
      & WdT(npdim,c
        real*8 NtK
      & Nt(nbandmi
      & DD(nbandmi
      & NORM1,NORM
         CHARACTER
        CHARACTER
         write(fil
      & ikw1,'.',i
c          write(f
         POTIM=1D0
         open(141,
         do i=1,nS
           Nt(i)=0
           Ntdt(i)c
           do j=1,
             NtKtd
             DD(i,
           enddo
         enddo
!---------------
! Overlap of "old
!---------------
             do i
             over
               do
             over
      &conjg(WT(k,c
               enc
              Nt(
c        print*,'N
             enddc
```

```
        print*,'Nt(i)=',Nt(i)
          enddo
!-----------------------------------------------------------------------------
 Overlap of "new wavecar" with other "new wavecar": <psi(t+dt)|psi(t+dt)>
!-----------------------------------------------------------------------------
          do i=nbandmin,nbandmax
            overlap=0D0
              do k=1,npw
                overlap=overlap+WdT(k,i,ikw1,ispin)*
      &conjg(WdT(k,i,ikw1,ispin))
              enddo
             Ntdt(i)=overlap
            print*,'Ntdt(i)=',Ntdt(i),Nt(i)
          enddo
!-----------------------------------------------------------------------------
 Overlap of "old wavecar" with "new wavecar": 1-st part of <psi(t+dt)|psi(t)>
!-----------------------------------------------------------------------------
         do i=nbandmin,nbandmax
            do j=nbandmin,nbandmax
            overlap=0D0
              do k=1,npw
                overlap=overlap+WdT(k,j,ikw1,ispin)*
      &conjg(WT(k,i,ikw,ispin))
              enddo
               NtKtdt(i,j)=overlap
          write(401,*) NtKtdt(i,j)
                print*,overlap
            enddo !j-cycle
          enddo ! i-cycle
           print*,'cycle 1',overlap
!-----------------------------------------------------------------
```

MATLAB: Reading Coupling Files

Group Meeting 6/14/2022

Adam Flesche

MATLAB & Input Files

- Two types are needed:
  - coupling.###
  - energy_pop
- These are used in the “correlation_v7.m” script
- This file must be modified to suit your system
  - The numerical range of states in energy_pop as well as the HOMO
  - The method which MATLAB uses to read coupling.### files

```
II=sqrt(-1);
HOMO=82
Omin=64
Omax=99
nO=Omax-Omin+1;
energy_pop=load('energy_pop');
e=energy_pop(:,2);
nu=energy_pop(:,1);


%for k=1:9;
%k
%file=['coupling.00',num2str(k)];
%c(:,:,k)=load(file);
%end;
%for k=10:15;%99;
%k
%file=['coupling.0',num2str(k)];
%c(:,:,k)=load(file);
%end;
for k=106:605;
k
file=['coupling.',num2str(k)];
c(:,:,k)=load(file);
end;
CORR=zeros(size(c));
eCORR=CORR;
```

Reading energy_pop

- MATLAB needs you to specify the following:
  - Omin, the lowest orbital in energy_pop
  - Omax, the highest orbital in energy_pop
  - HOMO
- Find these manually in photon or cori:
  > more energy_pop

```
II=sqrt(-1);
HOMO=82
Omin=64
Omax=99
no=Omax-Omin+1;
energy_pop=load('energy_pop');
e=energy_pop(:,2);
nu=energy_pop(:,1);
```

Reading coupling.### Files

- The script reads coupling files as “coupling.” and grabs the number in the filename “###”
- MATLAB struggles with reading numbers in the filename:
  - “coupling.023” would read as “023”, MATLAB does not understand this as 23.
  - “coupling.009” would read as “009”, etc.

```
%for k=1:9;
%k
%file=['coupling.00',num2str(k)];
%c(:,:,k)=load(file);
%end;
%for k=10:15;%99;
%k
%file=['coupling.0',num2str(k)];
%c(:,:,k)=load(file);
%end;
for k=106:605;
k
file=['coupling.',num2str(k)];
c(:,:,k)=load(file);
end;
CORR=zeros(size(c));
eCORR=CORR;
```

Reading coupling.### cont.

- The script may be run three separate times for coupling files ending in:
  - 001-009
  - 010-099
  - 100-999

```
for k=1:9;
k
file=['coupling.00',num2str(k)];
c(:,:,k)=load(file);
end;
```

```
for k=10:99;
k
file=['coupling.0',num2str(k)];
c(:,:,k)=load(file);
end;
```

```
for k=100:999;
k
file=['coupling.',num2str(k)];
c(:,:,k)=load(file);
end;
```

- If you don't have 999 coupling files, just specify how many you have.

…but that would be impressive if you did.

Input Files (all must be in the same directory)

- coupling.xxx
- energy_pop
- correlation_v7.m

```
II=sqrt(-1);
HOMO=316
Omin=296
Omax=337
nO=Omax-Omin+1;
energy_pop=load('energy_pop');
e=energy_pop(:,2);
nu=energy_pop(:,1);
```

```
% TIME STEPS < 10
for k=1:9;
k
file=['coupling.00',num2str(k)];
c(:,:,k)=load(file);
end;
% 10 <= TIME STEPS < 100
for k=10:61;%99;
k
file=['coupling.0',num2str(k)];
c(:,:,k)=load(file);
end;

% TIME STEPS > 100
for k=120:149;
k
file=['coupling.',num2str(k)];
% STORES COUPLING AS ARRAY, THIRD INDEX = TIME STEP
c(:,:,k)=load(file);
end;
```

Calculating RRR

```
% TTT = (high k) - 1
TTT=61-1;
% time1 = 1:TTT
for time1=1:60;
time1
%   time2 = time1:(high time1) + 1
    for time2=time1:61;
        for i=1:nO;
            for j=1:nO;
%               AUTO CORRELATION OF THE COUPLINGS
                CORR(i,j,time2-time1+1)=CORR(i,j,time2-time1+1)+c(i,j,time1)*c(i,j,time2);
%               APPROX INTEGRAL FOR REDFIELD TENSOR
               eCORR(i,j,time2-time1+1)=eCORR(i,j,time2-time1+1)+c(i,j,time1)*c(i,j,time2)*exp(II*(e(i)-e(j))*(time2-time1));
            end;
        end;
    end;
end;

RRR(:,:)=CORR(:,:,1)/TTT;mesh(RRR);
save RRR RRR -ASCII
```

$$\mathrm{M}_{ijij}(\tau) = \frac{1}{T}\int_0^T V_{ij}(t+\tau)V_{ij}(t)dt$$

$$\mathrm{R}_{iijj} = \frac{1}{T}\int_0^T M_{ijij}(\tau)e^{-i\omega_{ij}\tau}dt$$

Convert Couplings into RRR for Spin Polarized Case

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June 2022

Required files to run correlation.m file:

- energy_pop
- coupling.XXX files → In each directory unzip the coupling files using: gunzip coupling*

# of HOMO orbital
Range of desired orbitals

Importing energy_pop file data

```
II=sqrt(-1);
HOMO=196
Omin=172
Omax=213
nO=Omax-Omin+1;
energy_pop=load('energy_pop');
e=energy_pop(:,2);
ooo=energy_pop(:,1);
 [Nmax dum]=size(ooo);
Nmax2=Nmax*Nmax;
```

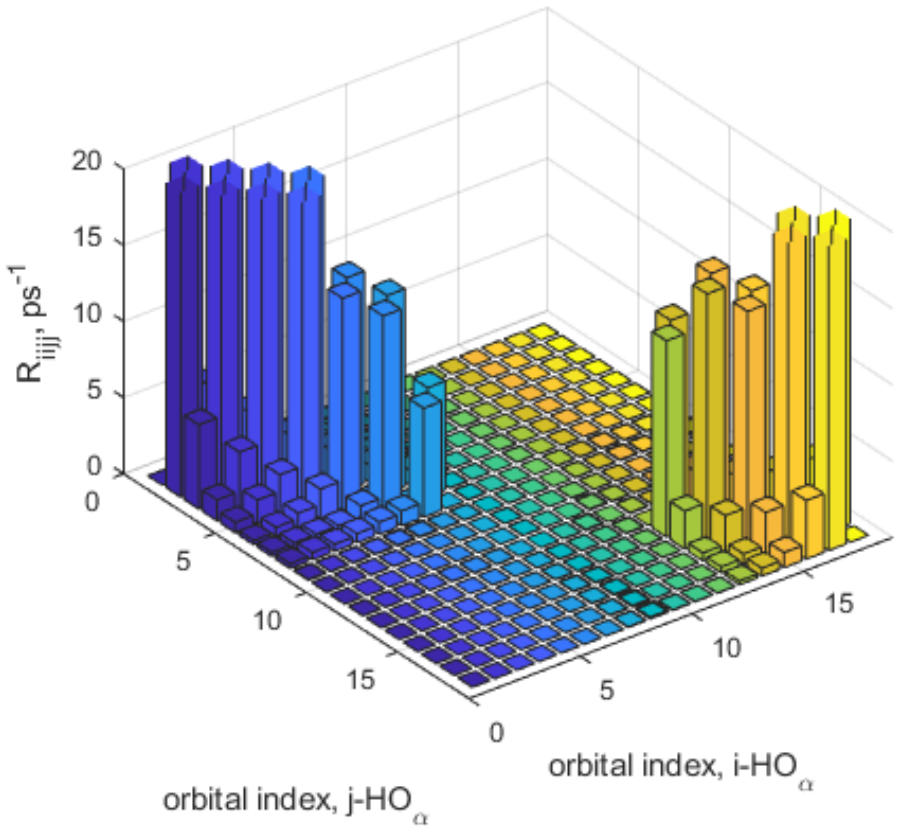
```
for k=1:9;
k
file=['coupling.00',num2str(k)];
c(:,:,k)=load(file);
end;
for k=10:99;
k
file=['coupling.0',num2str(k)];
c(:,:,k)=load(file);
end;
for k=100:360;
k
file=['coupling.',num2str(k)];
c(:,:,k)=load(file);
end;
CORR=zeros(size(c));
eCORR=CORR;
```

Importing coupling files

```
TTT=359;
for time1=1:359;
time1
    for time2=time1:360;
        for i=1:nO;
            for j=1:nO;
```

Number of steps

✓ After running MATLAB successfully, RRR file will be generated.



✓ You need to repeat the same procedure for spin beta component in its directory.

RRR file:

RRR

0.0000000e+00	2.8429023e-02	8.3659128e-03	2.3020007e-03	9.1265931e-04	4.0467340e-04	2.5230659e-04	1.6223806e-04	1.2112691e-04	8.9128613e-05	1.0022953e-04	7.8530511e-05	6.3766718e-0
2.8429023e-02	0.0000000e+00	2.0559988e-02	6.6333547e-03	2.2669133e-03	8.3254438e-04	5.1879147e-04	3.2260759e-04	2.0678220e-04	1.1195292e-04	9.1837161e-05	7.5643802e-05	8.6433007e-0
8.3659128e-03	2.0559988e-02	0.0000000e+00	2.4415721e-02	5.3787534e-03	2.1533160e-03	1.0337633e-03	4.3066133e-04	2.8901966e-04	1.5444143e-04	1.3048904e-04	8.8675643e-05	7.2412306e-0
2.3020007e-03	6.6333547e-03	2.4415721e-02	0.0000000e+00	2.6394693e-02	8.0462329e-03	2.6645171e-03	8.3133679e-04	4.1306855e-04	2.6565153e-04	1.9293450e-04	1.6062489e-04	1.1480777e-0
9.1265931e-04	2.2669133e-03	5.3787534e-03	2.6394693e-02	0.0000000e+00	2.3117055e-02	4.5076241e-03	2.4973686e-03	9.6850248e-04	5.6223329e-04	3.3561359e-04	2.0089424e-04	1.6878206e-0
4.0467340e-04	8.3254438e-04	2.1533160e-03	8.0462329e-03	2.3117055e-02	0.0000000e+00	2.5069754e-02	6.9097569e-03	1.9973311e-03	1.5459024e-03	7.8168486e-04	2.5944842e-04	2.3950524e-0
2.5230659e-04	5.1879147e-04	1.0337633e-03	2.6645171e-03	4.5076241e-03	2.5069754e-02	0.0000000e+00	2.4458101e-02	5.2129885e-03	1.8269919e-03	1.3341168e-03	4.7441147e-04	2.3958345e-0
1.6223806e-04	3.2260759e-04	4.3066133e-04	8.3133679e-04	2.4973686e-03	6.9097569e-03	2.4458101e-02	0.0000000e+00	2.4365948e-02	3.7805874e-03	2.5360626e-03	9.6393559e-04	4.9087553e-0
1.2112691e-04	2.0678220e-04	2.8901966e-04	4.1306855e-04	9.6850248e-04	1.9973311e-03	5.2129885e-03	2.4365948e-02	0.0000000e+00	2.3226061e-02	6.7023897e-03	2.1237139e-03	8.4776411e-0
8.9128613e-05	1.1195292e-04	1.5444143e-04	2.6565153e-04	5.6223329e-04	1.5459024e-03	1.8269919e-03	3.7805874e-03	2.3226061e-02	0.0000000e+00	2.1316136e-02	3.7955575e-03	2.2253443e-0
1.0022953e-04	9.1837161e-05	1.3048904e-04	1.9293450e-04	3.3561359e-04	7.8168486e-04	1.3341168e-03	2.5360626e-03	6.7023897e-03	2.1316136e-02	0.0000000e+00	2.2544681e-02	6.8657380e-0
7.8530511e-05	7.5643802e-05	8.8675643e-05	1.6062489e-04	2.0089424e-04	2.5944842e-04	4.7441147e-04	9.6393559e-04	2.1237139e-03	3.7955575e-03	2.2544681e-02	0.0000000e+00	2.3005528e-0
6.3766718e-05	8.6433007e-05	7.2412306e-05	1.1480777e-04	1.6878206e-04	2.3950524e-04	2.3958345e-04	4.9087553e-04	8.4776411e-04	2.2253443e-03	6.8657380e-03	2.3005528e-02	0.0000000e+0
5.5343804e-05	6.8037081e-05	6.1659882e-05	1.2531397e-04	1.1649468e-04	1.3343484e-04	1.9357684e-04	3.5816156e-04	3.8489475e-04	7.3626422e-04	1.9443181e-03	4.6554077e-03	2.1343622e-0
4.9443277e-05	6.3574522e-05	9.4537418e-05	9.5776732e-05	1.1029827e-04	1.3374344e-04	1.3589973e-04	2.0079142e-04	2.7665318e-04	5.2867422e-04	1.5700602e-03	2.6453209e-03	5.5062215e-0
3.9182451e-05	4.0739069e-05	5.7832575e-05	6.7855506e-05	7.2066321e-05	1.0000037e-04	1.0209782e-04	1.5605554e-04	1.5502351e-04	2.2219532e-04	5.6436095e-04	7.8492069e-04	2.3593865e-0
3.0931425e-05	3.8982003e-05	5.0511534e-05	5.6359652e-05	7.2575162e-05	7.8576224e-05	9.1584952e-05	9.5227373e-05	1.1744302e-04	2.2483502e-04	2.8523792e-04	5.4052413e-04	8.0817226e-0
3.9357666e-05	4.7946040e-05	5.9614152e-05	7.6675791e-05	7.5606584e-05	7.9851786e-05	8.8671391e-05	1.1004948e-04	1.0459018e-04	1.2348767e-04	2.0218582e-04	2.9659688e-04	4.8514200e-0
4.3246167e-05	3.8720903e-05	5.8648026e-05	7.7626698e-05	7.2296713e-05	7.1818429e-05	7.7949268e-05	7.4486558e-05	9.3378075e-05	9.3743153e-05	1.6408647e-04	2.0100708e-04	2.8101946e-0
4.6629703e-05	4.7442638e-05	7.0063609e-05	6.7613925e-05	8.6950787e-05	7.5578265e-05	5.4335493e-05	9.3611718e-05	9.9377205e-05	1.1229484e-04	1.2957691e-04	1.3822610e-04	1.7285210e-0
5.5151330e-05	5.7054453e-05	8.5628450e-05	6.4056179e-05	8.9957406e-05	1.4719118e-04	1.1866230e-04	1.3407207e-04	1.1949603e-04	1.4618355e-04	2.3007358e-04	1.4664352e-04	1.7686853e-0
8.9411134e-05	1.0937613e-04	9.0498864e-05	1.0248375e-04	1.1406297e-04	1.2876089e-04	2.1327338e-04	1.7983043e-04	1.6655015e-04	2.2105422e-04	2.6154514e-04	2.3558679e-04	2.0531064e-0
1.2249551e-04	1.2244292e-04	1.6201562e-04	1.7521184e-04	2.0978272e-04	2.1874452e-04	1.5426692e-04	2.3830070e-04	1.3941026e-04	1.9546554e-04	1.6948212e-04	2.1168459e-04	2.9408595e-0
5.2702834e-04	6.4276296e-04	8.7730641e-04	5.0884721e-04	5.0415269e-04	4.8695720e-04	4.8438111e-04	4.2868033e-04	3.3866133e-04	3.5990912e-04	3.9208165e-04	3.6786115e-04	4.5622974e-0
5.4028596e-05	6.0367577e-05	3.9064192e-05	4.7410877e-05	4.4805690e-05	4.9972924e-05	7.1926726e-05	5.5836751e-05	4.9195205e-05	4.9270295e-05	6.1415109e-05	6.6336443e-05	5.5676422e-0
1.0461847e-04	7.3223972e-05	5.1334040e-05	7.9903428e-05	6.5473229e-05	6.3273802e-05	8.6842235e-05	5.3350255e-05	4.3079348e-05	3.5488339e-05	2.7925003e-05	2.8426903e-05	3.9884034e-0
4.8632045e-06	5.6652743e-06	4.1831094e-06	5.7823721e-06	5.5165715e-06	6.7413616e-06	5.6496851e-06	5.8750446e-06	5.9455829e-06	4.8963822e-06	6.4046538e-06	6.0313880e-06	5.4822890e-0
6.7522098e-06	7.6417379e-06	9.5241391e-06	1.2045869e-05	1.1259587e-05	1.0703767e-05	1.7506676e-05	1.5529541e-05	1.8740504e-05	1.7646028e-05	1.6066903e-05	1.7513262e-05	1.5946274e-0
4.4157905e-06	4.1783792e-06	3.8026790e-06	3.0697702e-06	4.7488411e-06	7.1178788e-06	4.6011132e-06	4.5885403e-06	4.9836079e-06	6.8324122e-06	5.4101264e-06	6.2096446e-06	5.8862135e-0
5.2454754e-06	4.8365660e-06	4.6857351e-06	5.1937358e-06	5.7655296e-06	4.6358613e-06	5.5831620e-06	5.5744597e-06	5.5677736e-06	6.9420868e-06	7.9708191e-06	8.0966135e-06	6.6737925e-0
7.0113348e-06	5.1402579e-06	6.6640265e-06	7.4393734e-06	6.1931955e-06	6.3918726e-06	7.3022447e-06	7.2564817e-06	5.8444799e-06	6.1384526e-06	7.2813319e-06	6.8606362e-06	5.3126346e-0
9.1160289e-06	7.7561646e-06	7.2434066e-06	6.0514046e-06	6.7227205e-06	6.1041480e-06	6.3895741e-06	5.9123957e-06	5.3514076e-06	5.9814561e-06	5.5700634e-06	5.2720505e-06	4.8365627e-0
5.3730621e-06	6.8779587e-06	6.1614027e-06	5.5784038e-06	6.9191793e-06	5.3642936e-06	5.7886426e-06	6.5707557e-06	5.6777603e-06	6.3121398e-06	4.0719733e-06	4.4736330e-06	3.8717284e-0
6.4883796e-06	5.3847212e-06	5.2003735e-06	7.0439939e-06	5.9602249e-06	5.4977779e-06	6.9166127e-06	7.2801194e-06	7.0731677e-06	5.0996012e-06	5.4167270e-06	4.1811458e-06	3.7403966e-0
5.5906505e-06	6.0305597e-06	5.3708046e-06	6.4028490e-06	6.6508546e-06	6.0746404e-06	5.7673245e-06	4.9744093e-06	5.6524805e-06	4.7495335e-06	5.8706387e-06	4.9637765e-06	5.7016289e-0
4.6077732e-06	5.3189365e-06	5.3915533e-06	4.5090043e-06	4.8925912e-06	5.4087836e-06	6.2746641e-06	5.2490581e-06	5.9208007e-06	5.6237898e-06	6.5283942e-06	6.0466150e-06	5.0666037e-0
4.5053604e-06	5.3057060e-06	5.9627369e-06	5.4532739e-06	5.8452255e-06	4.2155507e-06	4.7241843e-06	5.6960949e-06	6.7336721e-06	5.4309643e-06	6.0841825e-06	6.1880933e-06	5.8508114e-0
6.7840856e-06	5.9407708e-06	7.2029199e-06	6.7447690e-06	7.1618286e-06	7.3700563e-06	6.6117745e-06	5.8498243e-06	6.9434251e-06	7.4344461e-06	7.7898607e-06	8.1272398e-06	7.5868155e-0
8.3502297e-06	7.0000942e-06	6.4441825e-06	6.4940045e-06	6.4305015e-06	6.0892962e-06	4.4916103e-06	4.7897525e-06	5.2306791e-06	5.7959289e-06	6.2435282e-06	6.0856466e-06	5.1212333e-0
9.1968824e-06	5.7568078e-06	8.2307411e-06	6.7670344e-06	6.9908353e-06	6.3230897e-06	6.6407073e-06	5.8109758e-06	7.1257677e-06	6.2113536e-06	6.7893559e-06	5.3762668e-06	4.8754596e-0
1.1757351e-05	1.0981647e-05	9.5731794e-06	9.2920260e-06	8.4061560e-06	7.4320237e-06	6.2424036e-06	5.5265371e-06	5.1638304e-06	6.4080449e-06	6.0585739e-06	6.3277874e-06	4.7869010e-0
1.0128478e-05	7.9469307e-06	7.4513865e-06	7.5967710e-06	8.3217529e-06	7.0018326e-06	5.9631160e-06	7.3571835e-06	8.0493010e-06	6.5325952e-06	5.9111506e-06	8.1323533e-06	7.9323103e-0

Introduction to the Autocorrelation Function

Summer 2022 Computational Chemistry Skills Presentation

6/14/2022

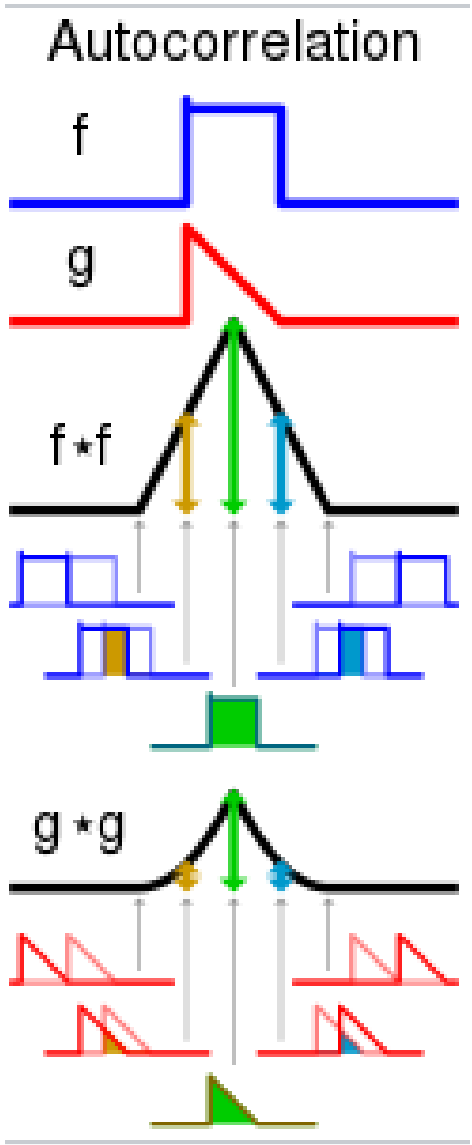
Hadassah B. Griffin

Overview of Calculations

- Heat Model
- Molecular Dynamics (MD)
- Nonadiabatic Coupling Calculations
- **Autocorrelation Function Calculations**
- Redfield Tensor
- Observables

Autocorrelation Functions

- Correlation Functions (generic): describe how different quantities compare at a specific point in space or time
  - Example: convolution
- Autocorrelation Function: a correlation function where a quantity is compared with itself



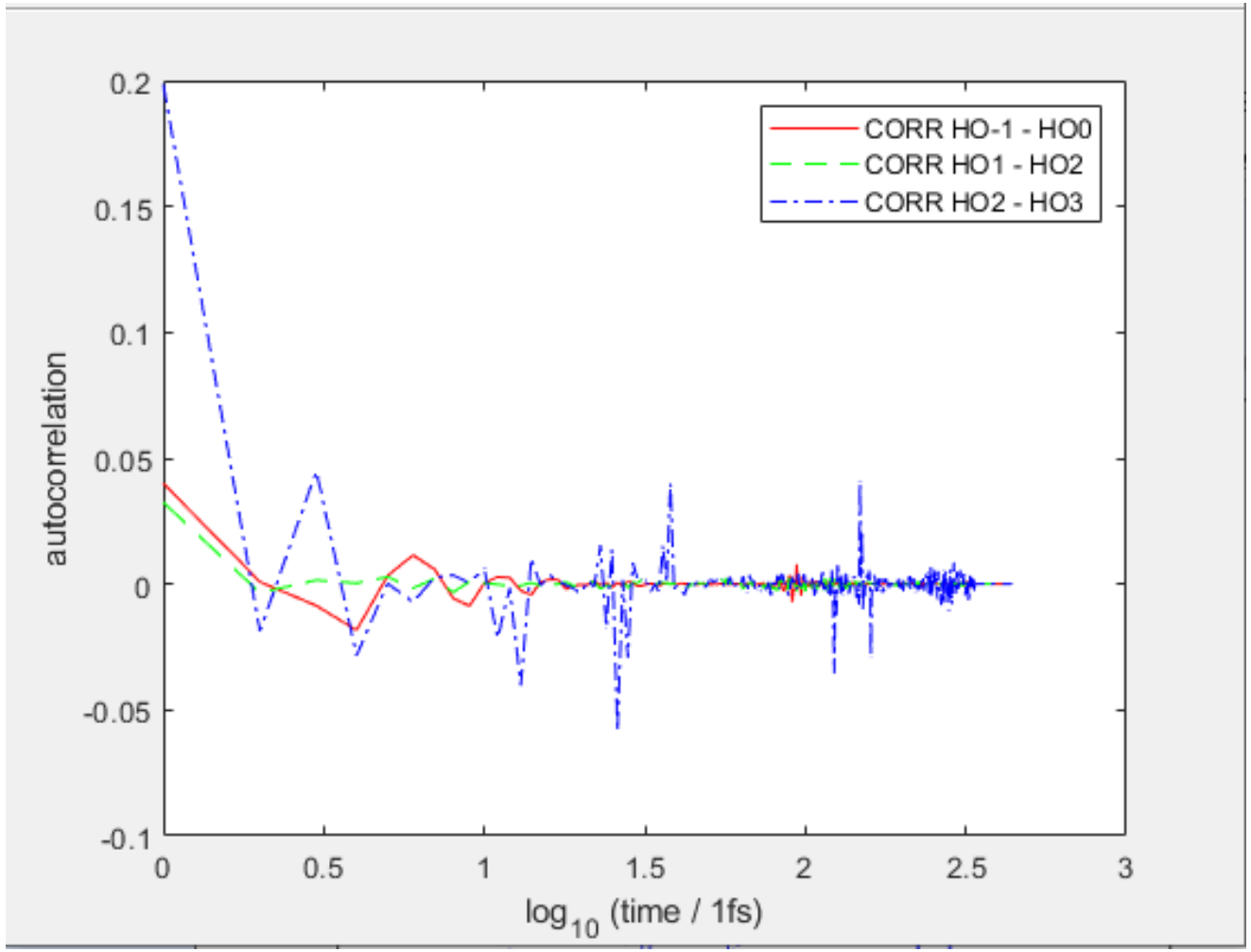
Autocorrelation for Nonadiabatic Couplings

- Autocorrelation function:
  - $M_{ijkl}(\tau) = \frac{1}{T}\int_0^T V_{ij}(t + \tau)\, V_{kl}(t)\, dt$
    - T: duration of the trajectory of MD
    - Ijkl: indices for the coupling time snapshots
    - Note the averaging
  - Provides first order correction approximation for the of adiabatic couplings of the electrons for time dependent perturbation theory and a second order correction perturbation with respect to the electron-nuclear interaction

Fourier Transform

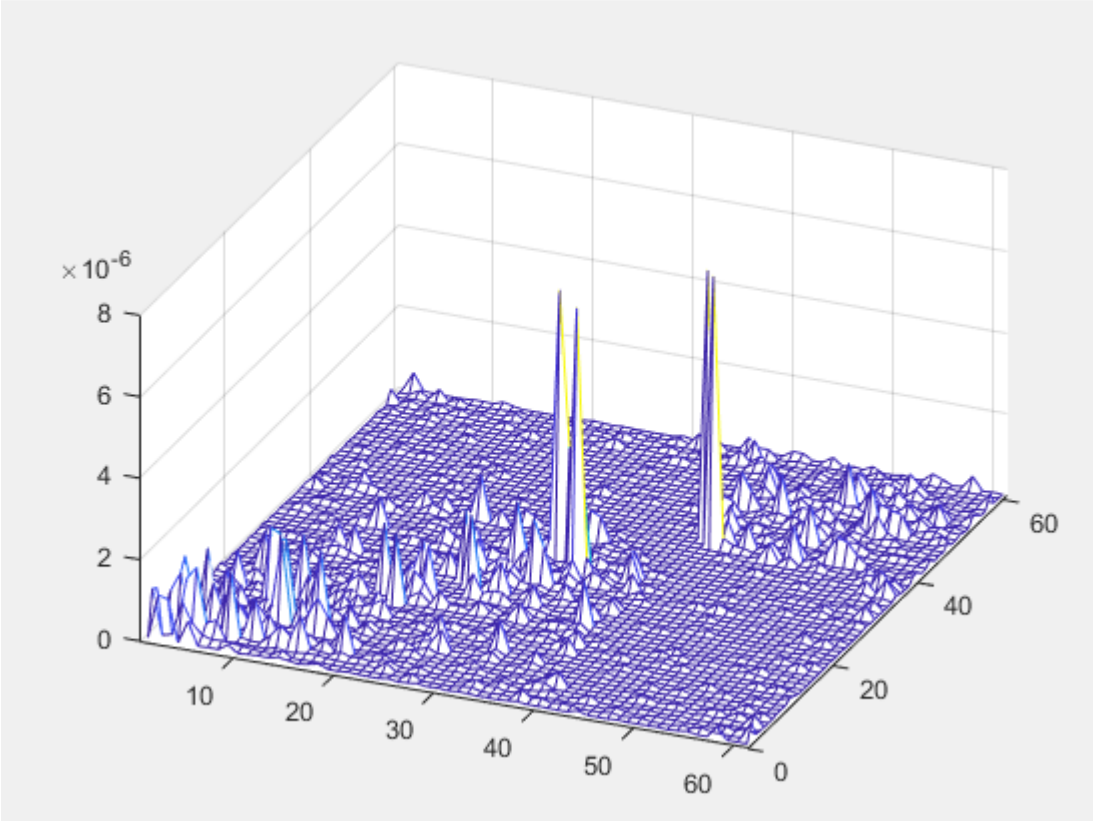
- Fourier Transform of autocorrelation function:
  - $\Gamma^{+}_{\sigma,ijkl} = \frac{1}{T}\int_0^T e^{-i\,\omega_{ij}t} M_{\sigma,ijkl}(t)\ d\tau$
  - $\Gamma^{-}_{\sigma,ijkl} = \frac{1}{T}\int_0^T e^{-i\,\omega_{kl}t} M_{\sigma,ijkl}(t)\ d\tau$
- Fourier transform pieces used to provide components of the Redfield Tensor
- Redfield Tensor then used to compute electron dynamics

Correlation of HOMO-1 through HOMO+3

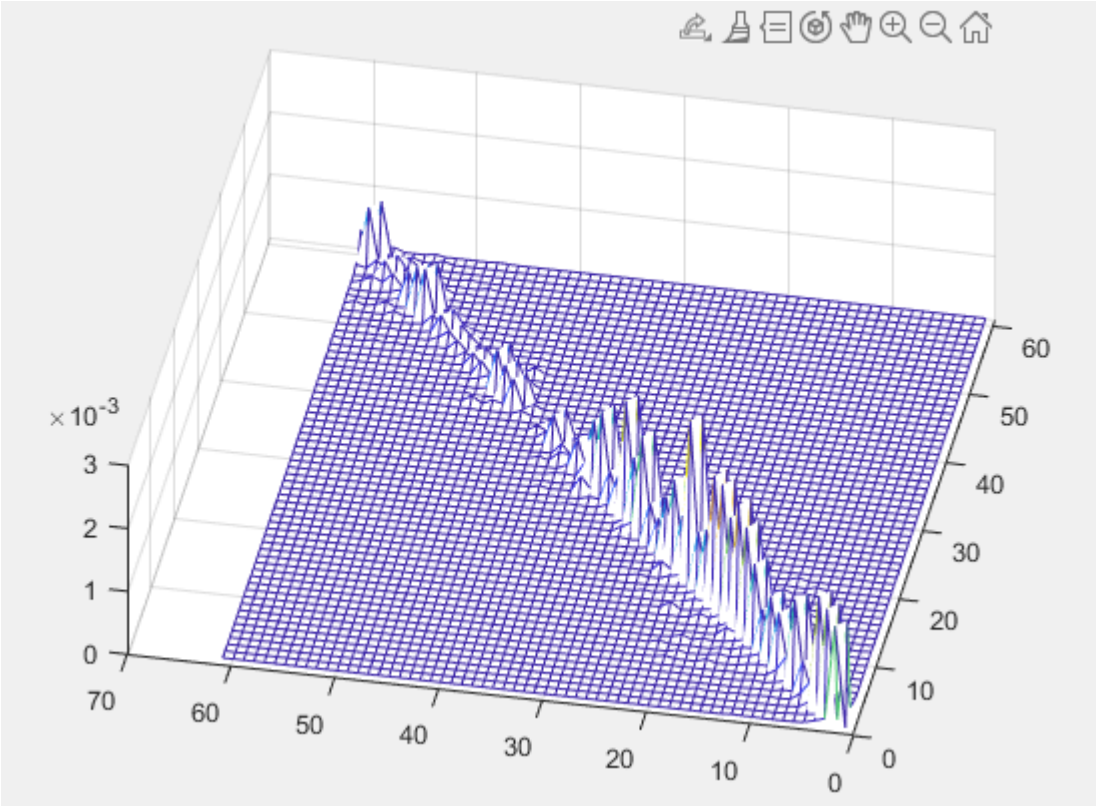


Visualization of Autocorrelation Function Elements as Matrix Elements of Redfield Tensor (Model: Cd33Se33 + Pb16Se16 Nanocrystal)

- **p100 – p105**



- **p100 – p442**



Cited Sources

- Image and general definition of autocorrelation credits: https://en.wikipedia.org/wiki/Autocorrelation
- Equations and concepts:
  - "Spin Unrestricted Excited State Relaxation Study of Vanadium(IV)-Doped Anatase", Stephanie J. Jensen, 2016
  - Summer 2018 Skill presentation, Aaron Forde

Definition of the Redfield Tensor

As made by: ~/bin/MATLAB/correlation_v7.m

Landon Johnson

Nonadiabatic Couplings

$$V_{ij}(t) = -\frac{i\hbar}{\Delta t}\int d\vec{r}\,\varphi_i^*\left(\vec{r},\left\{\vec{R}_I(t)\right\}\right)\varphi_j\left(\vec{r},\left\{\vec{R}_I(t+\Delta t)\right\}\right)$$

“Overlap” of orbitals i and j as the nuclei move around

Autocorrelation Function

$$M_{ijkl}(\tau) = \int_0^{t_{max}-\tau} dt V_{ij}(t+\tau) V_{kl}(t)$$

This value is high if overlap between these orbitals usually leads to overlap between these orbitals after a delay of τ

$M_{ijij}(\tau)$ is high for some $\tau >> 0$ $\Longrightarrow$ orbitals i and j tend to overlap periodically with a period of τ X

$M_{ijij}(\tau)$ drops to ≈ 0 quickly $\Longrightarrow$ orbitals i and j overlap at random times, not periodically ✓

τ $\quad V_{ij}(t) \quad V_{ij}(t+\tau)$

```
TTT=99-1;
for time1=1:98;
time1
    for time2=time1:99;
        for i=1:nO;
            for j=1:nO;

                CORR(i,j,time2-time1+1)=CORR(i,j,time2-time1+1)+c(i,j,time1)*c(i,j,time2);
               eCORR(i,j,time2-time1+1)=eCORR(i,j,time2-time1+1)+c(i,j,time1)*c(i,j,time2)*exp(II*(e(i)-e(j))*(time2-time1));

            end;
        end;
    end;
   %RED(:,:)=RED(:,:)+CORR(:,:,time2-time1+1);
end;
```

Autocorrelation Function

$$M_{ijkl}(\tau) = \int_0^{t_{max}-\tau} dt V_{ij}(t+\tau) V_{kl}(t)$$

The autocorrelation function will often display oscillatory and/or decaying behavior, i.e. $M_{ijij}(\tau) \approx \cos(\omega\tau)\exp(-\gamma\tau)$ for some frequency ω and decay rate γ

$\omega \gg \gamma \Longrightarrow$ "monochromatic," FT will have strong frequency dependence, i.e. $M(\omega)$ depends strongly on all values of τ X

$\gamma \gg \omega \Longrightarrow$ "white noise," FT will be ~constant, i.e. $M(\omega)$ =constant, so we only really care about $M(\tau = 0)$ ✓

Transition Rates

$$\Gamma^{+}_{ijkl} = \int d\tau\, M_{ijkl}(\tau)\exp(-i\omega_{kl}\tau)$$

$$\Gamma^{-}_{ijkl} = \int d\tau\, M_{ijkl}(\tau)\exp\left(-i\omega_{ij}\tau\right)$$

ω_{kl} is the angular frequency of a photon with the same energy as the energy gap between orbitals k and l

Note that $\Gamma^{+}_{ijij} = \Gamma^{-}_{ijij}$

Also note that if $M_{ijij}(\tau)$ drops to ≈ 0 quickly, then $\Gamma^{+}_{ijij} \approx M_{ijij}(0)$

Redfield Tensor

$$R_{ijkl} = \Gamma^{+}_{ijkl} + \Gamma^{-}_{ijkl} - \cancelto{0}{\delta_{ij} \sum_{m} \Gamma^{+}_{kmml}} - \cancelto{0}{\delta_{kl} \sum_{m} \Gamma^{-}_{immj}}$$

Note that for R_{ijij} with $i \neq j$ (i.e. transitions between two DIFFERENT orbitals), $\delta_{ij} = 0$, so $R_{ijij} \propto \Gamma^{+}_{ijij} \approx M_{ijij}(0)$

$$\overbrace{\qquad\qquad}^{R_{ijij}}\qquad \overbrace{\qquad\qquad\qquad\qquad}^{M_{ijij}(0)}$$

i j i j $\tau = 0$

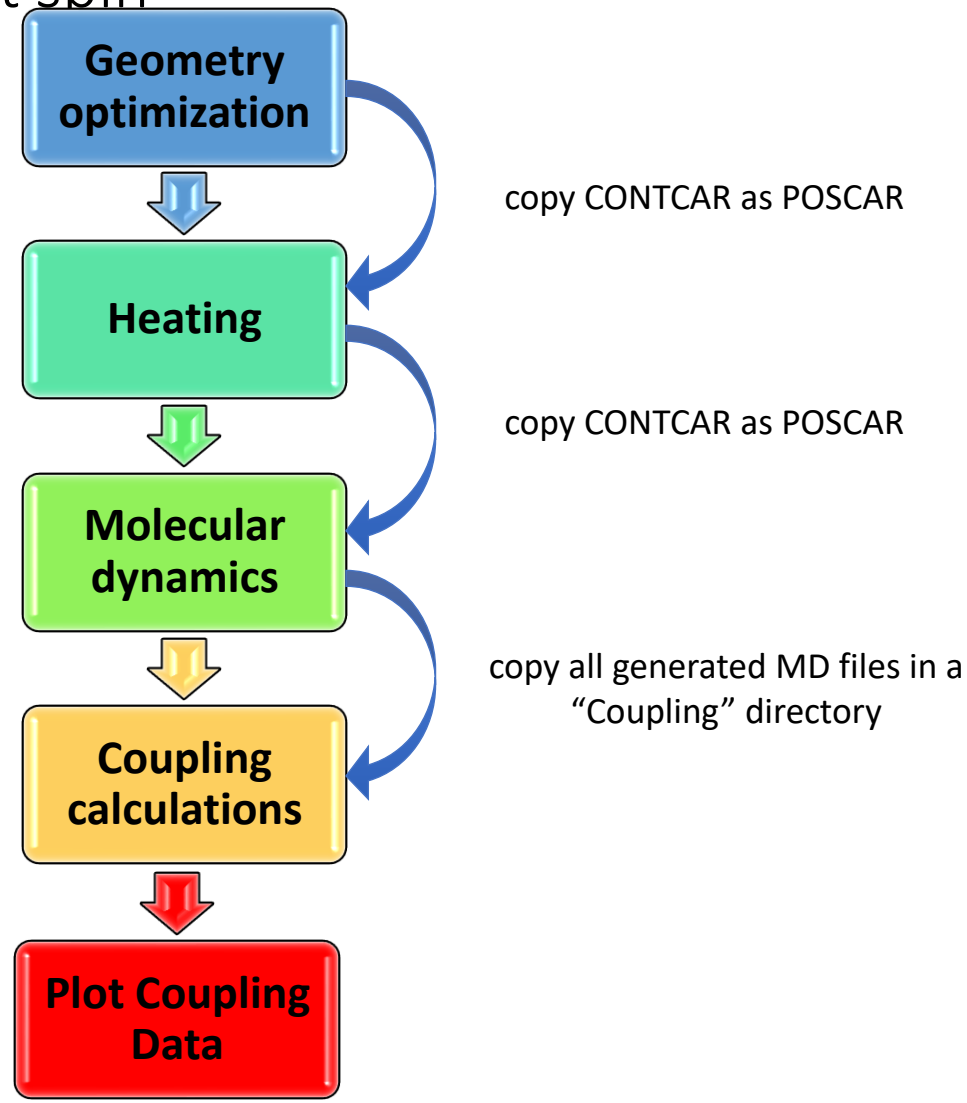
```
RRR(:,:)=CORR(:,:,1)/TTT;mesh(RRR);
```

Nonadiabatic couplings without spin

(Plot the Redfield tensor elements and correlation function)

Summer 2022

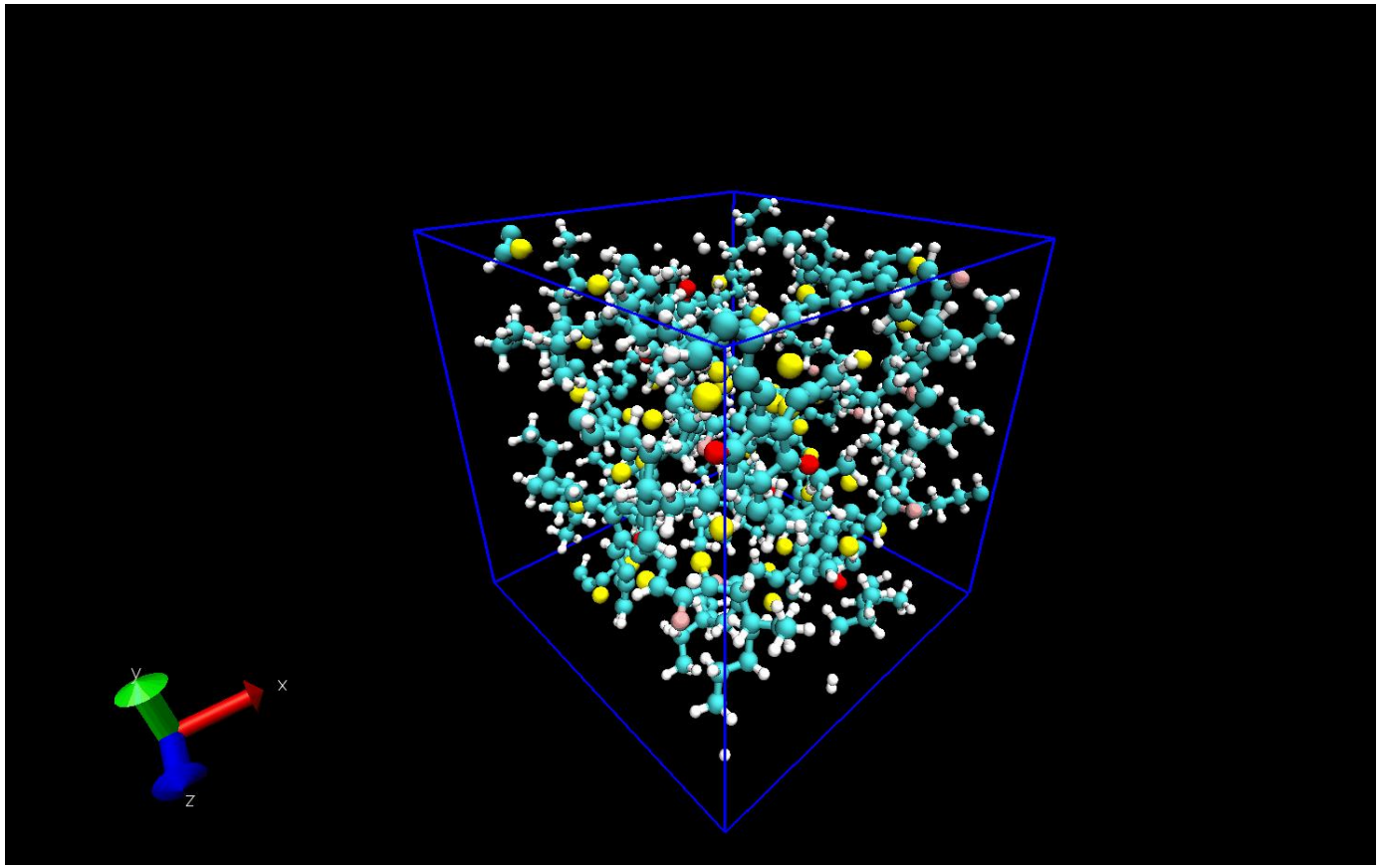
Nonadiabatic couplings without spin



Nonadiabatic couplings without spin

- **Case of study: a condensed 3D model for PM6 conjugated polymer**

gif



Nonadiabatic couplings without spin

- **What do we need to start the visualization:**

❑ **The “energy_pop” file:**

E:\PhD Papers\9_MD_DFT\Results\PM6\COUPLINGS\energy_pop - Notepad++

File Edit Search View Encoding Language Settings Tools Macro Run

VASP Commends.txt | energy_pop

4	1242	-2.0024	2.00000
5	1243	-1.9964	2.00000
6	1244	-1.9858	2.00000
7	1245	-1.9810	2.00000
8	1246	-1.9540	2.00000
9	1247	-1.9438	2.00000
10	1248	-1.9313	2.00000
11	1249	-1.9202	2.00000
12	1250	-1.8989	2.00000
13	1251	-1.8818	2.00000
14	1252	-1.8572	2.00000
15	1253	-1.8537	2.00000
16	1254	-1.7728	2.00000
17	1255	-1.7183	2.00000
18	1256	-1.6238	2.00000
19	1257	-1.5502	2.00000
20	1258	-1.5468	2.00000
21	1259	-1.4835	2.00000
22	1260	-1.4775	2.00000
23	1261	-1.4472	2.00000
24	1262	-1.3816	2.00000
25	1263	-1.3042	2.00000
26	1264	-1.2625	2.00000
27	1265	-1.1599	2.00000
28	1266	-1.1378	2.00000
29	1267	-1.0200	2.00000
30	1268	-1.0057	2.00000
31	1269	-0.9160	2.00000
32	1270	0.2874	0.00000
33	1271	0.3649	0.00000
34	1272	0.3715	0.00000
35	1273	0.4277	0.00000
36	1274	0.4535	0.00000
37	1275	0.5102	0.00000
38	1276	0.5503	0.00000
39	1277	0.5834	0.00000
40	1278	0.6428	0.00000
41	1279	0.6553	0.00000
42	1280	0.6869	0.00000
43	1281	0.7273	0.00000
44	1282	1.0196	0.00000
45	1283	1.0484	0.00000
46	1284	1.0674	0.00000
47	1285	1.1233	0.00000

Normal text file

Nonadiabatic couplings without spin

- **What do we need to start the visualization:**

- ❑ **Having the coupling files "couplingXXX" in a same directory of you Matlab code:**

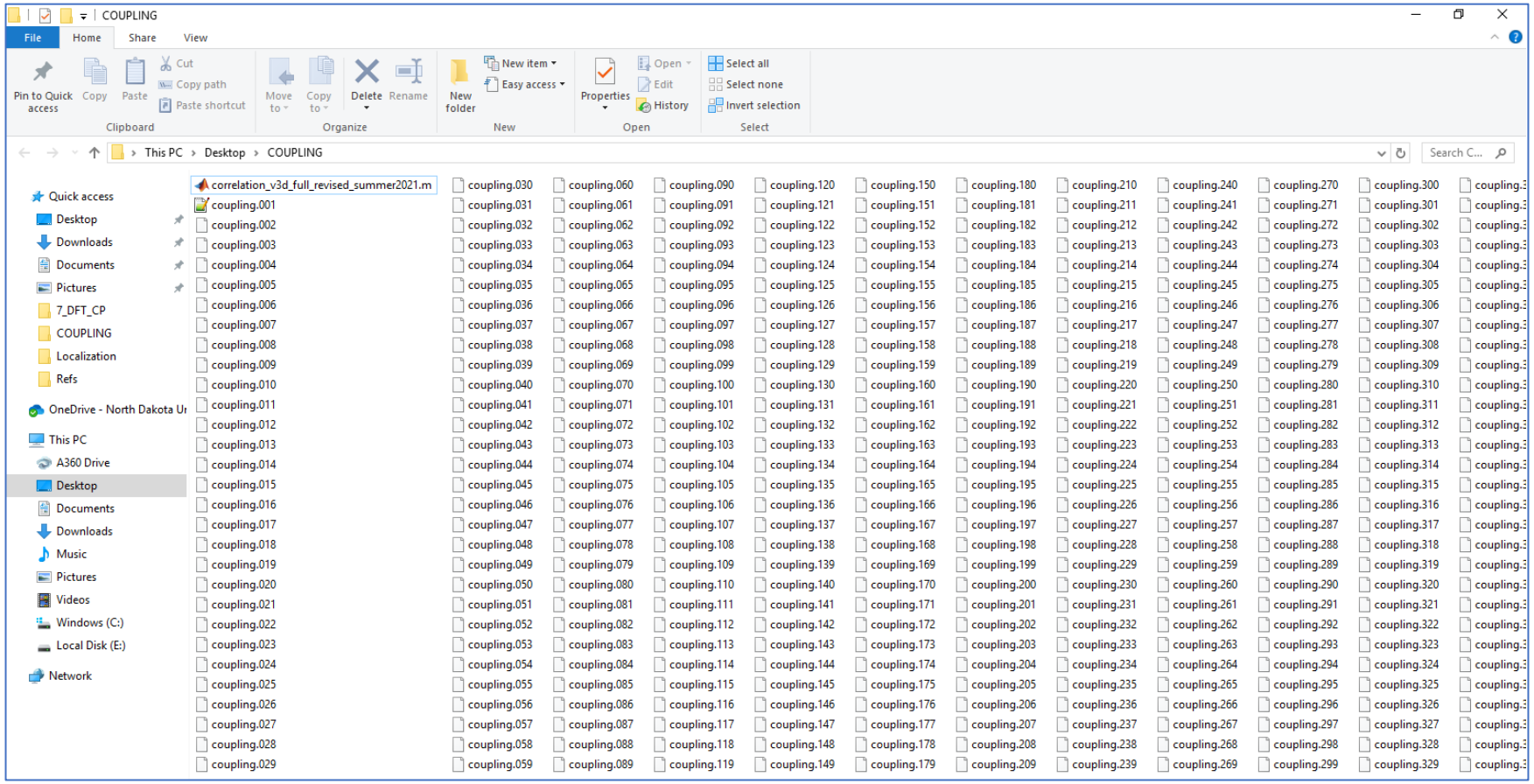
- ❑ **If you have zipped files (*.gz) on the cori or photon, you can unzip them via following commands:**

```
gzip -d *.gz
gzip -d coupling*

tar –xvzf  *.gz
```

Nonadiabatic couplings without spin

- **What do we need to start the visualization:**

❑ **Having the coupling files “couplingXXX” in a same directory of you Matlab code:**



Nonadiabatic couplings without spin

- **What do we need to start the visualization:**

❑ **Matlab script "correlation_v3d_full_revised_summer2021.m":**

Editor - E:\PhD Papers\9_MD_DFT\Results\PM6\COUPLINGS\correlation_v3d_full_revised_summer2021.m

correlation_v3d_full_revised_summer2021.m

```
% energy_pop file is needed
% as output, this program generates file RRR
clc;close all;
clear;

% II=sqrt(-1);

energy_pop=importdata('energy_pop');

% Number of time steps
TTT=400;

% Nubmer of Coupling files, usually around 1000
n_Coupling_files=400;


O_min=energy_pop(1,1) % Smallest orbital number in energy_pop
O_max=energy_pop(end,1) % Largest orbital number in energy_pop
n_Orbital=numel(energy_pop(:,1)) % Number of orbitals

% Finde the "HOMO" in energy_pop
for i=1:n_Orbital
    if energy_pop(i,3)<0.5
        HOMO=energy_pop(i-1,1)
        break
    end

end

```

E:\PhD Papers\9_MD_DFT\Results\PM6\COUPLINGS\energy_pop - Notepad++

File Edit Search View Encoding Language Settings Tools Macro Run

VASP Commends.txt | energy_pop

4	1242	-2.0024	2.00000
5	1243	-1.9964	2.00000
6	1244	-1.9858	2.00000
7	1245	-1.9810	2.00000
8	1246	-1.9540	2.00000
9	1247	-1.9438	2.00000
10	1248	-1.9313	2.00000
11	1249	-1.9202	2.00000
12	1250	-1.8989	2.00000
13	1251	-1.8818	2.00000
14	1252	-1.8572	2.00000
15	1253	-1.8537	2.00000
16	1254	-1.7728	2.00000
17	1255	-1.7183	2.00000
18	1256	-1.6238	2.00000
19	1257	-1.5502	2.00000
20	1258	-1.5468	2.00000
21	1259	-1.4835	2.00000
22	1260	-1.4775	2.00000
23	1261	-1.4472	2.00000
24	1262	-1.3816	2.00000
25	1263	-1.3042	2.00000
26	1264	-1.2625	2.00000
27	1265	-1.1599	2.00000
28	1266	-1.1378	2.00000
29	1267	-1.0200	2.00000
30	1268	-1.0057	2.00000
31	1269	-0.9160	2.00000
32	1270	0.2874	0.00000
33	1271	0.3649	0.00000
34	1272	0.3715	0.00000
35	1273	0.4277	0.00000
36	1274	0.4535	0.00000
37	1275	0.5102	0.00000
38	1276	0.5503	0.00000
39	1277	0.5834	0.00000
40	1278	0.6428	0.00000
41	1279	0.6553	0.00000
42	1280	0.6869	0.00000
43	1281	0.7273	0.00000
44	1282	1.0196	0.00000
45	1283	1.0484	0.00000
46	1284	1.0674	0.00000
47	1285	1.1233	0.00000

Normal text file

Nonadiabatic couplings without spin

- **Execute the Matlab file:**

❑ **In Matlab directory we should have:**

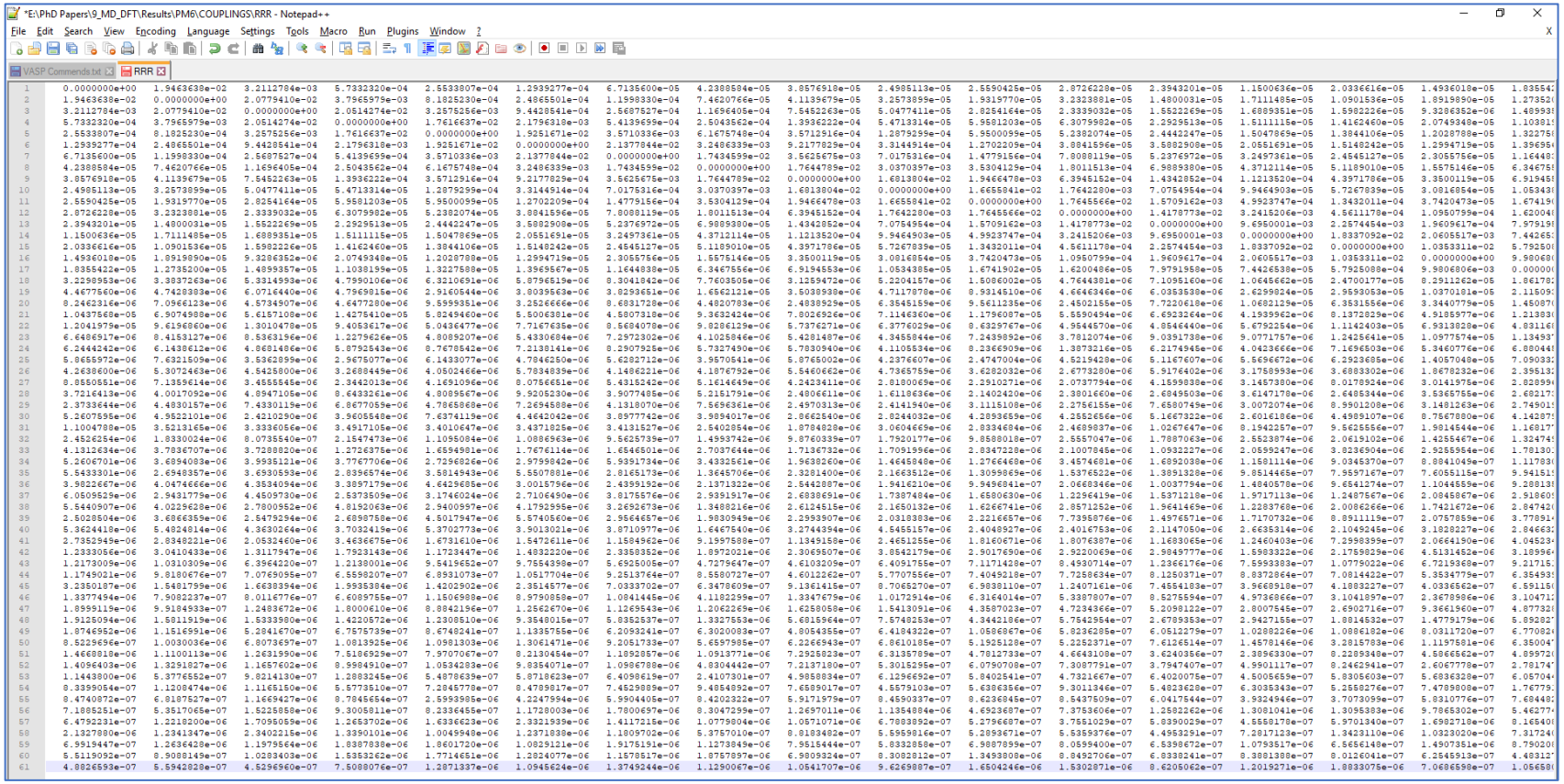
✓ energy_pop

✓ correlation_v3d_full_revised_summer2021.m

✓ coupling.xxx files

Nonadiabatic couplings without spin

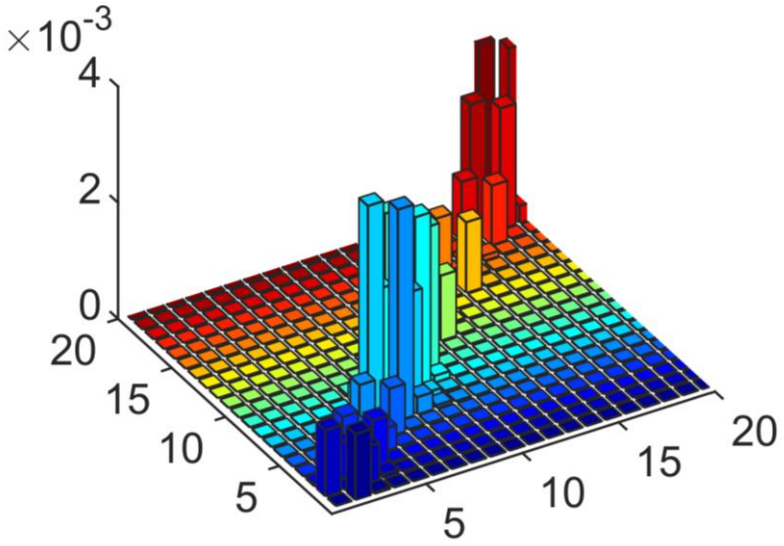
- **“RRR” file will be generated in your current directory at the end of calculations (this file include Redfield tensor):**
- This procedure (Matlab code) used all couplings files as input and provide RRR file as an output.

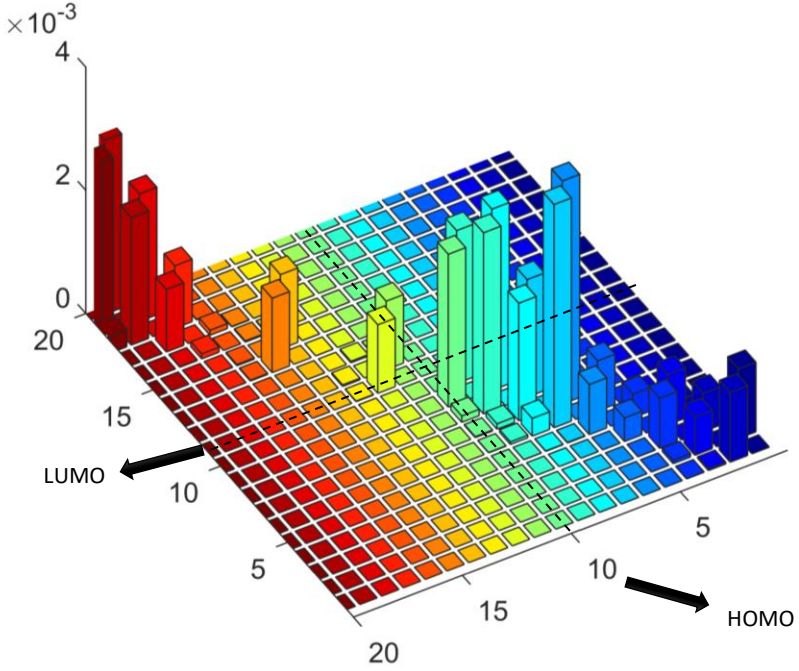


1	0.0000000e+00	1.9463638e-02	3.2112784e-03	5.7332320e-04	2.5533807e-04	1.2939277e-04	6.7135600e-05	4.2388584e-05	3.8576918e-05	2.4985113e-05	2.5590425e-05	2.8726228e-05	2.3943201e-05	1.1500636e-05	2.0336616e-05	1.4936018e-05	1.83554
2	1.9463638e-02	0.0000000e+00	2.0779410e-02	3.7965979e-03	8.1825230e-04	2.4865501e-04	1.1998330e-04	7.4620766e-05	4.1139679e-05	3.2573899e-05	1.9319770e-05	2.3323881e-05	1.4800031e-05	1.7111485e-05	1.0901536e-05	1.8919890e-05	1.27352
3	3.2112784e-03	2.0779410e-02	0.0000000e+00	2.0514274e-02	3.2575256e-03	9.4428541e-04	2.5687527e-04	1.1696405e-04	7.5452263e-05	5.0477411e-05	2.8254164e-05	2.3339032e-05	1.5522269e-05	1.6889351e-05	1.5982226e-05	9.3263652e-06	1.48993
4	5.7332320e-04	3.7965979e-03	2.0514274e-02	0.0000000e+00	1.7616637e-02	2.1796318e-03	5.4139699e-04	2.5043562e-04	1.3936222e-04	5.4713314e-05	5.9581203e-05	6.3079982e-05	2.2929513e-05	1.5111115e-05	1.4162460e-05	2.0749348e-05	1.10381
5	2.5533807e-04	8.1825230e-04	3.2575256e-03	1.7616637e-02	0.0000000e+00	1.9251671e-02	3.5710336e-03	6.1675748e-04	3.5712916e-04	1.2879299e-04	5.9500099e-05	5.2382074e-05	2.4442247e-05	1.5047869e-05	1.3844106e-05	1.2028788e-05	1.32275
6	1.2939277e-04	2.4865501e-04	9.4428541e-04	2.1796318e-03	1.9251671e-02	0.0000000e+00	2.1377844e-02	3.2486339e-03	9.2177829e-04	3.3144914e-04	1.2702209e-04	3.8841596e-05	3.5882908e-05	2.0551691e-05	1.5148242e-05	1.2994719e-05	1.39695
7	6.7135600e-05	1.1998330e-04	2.5687527e-04	5.4139699e-04	3.5710336e-03	2.1377844e-02	0.0000000e+00	1.7434599e-02	3.5625675e-03	7.0175316e-04	1.4779156e-04	7.8088119e-05	5.2376972e-05	3.2497361e-05	2.4545127e-05	2.3055756e-05	1.16448
8	4.2388584e-05	7.4620766e-05	1.1696405e-04	2.5043562e-04	6.1675748e-04	3.2486339e-03	1.7434599e-02	0.0000000e+00	1.7644789e-02	3.0370397e-03	3.5304129e-04	1.8011513e-04	6.9889380e-05	4.3712114e-05	5.1189010e-05	1.5575146e-05	6.34675
9	3.8576918e-05	4.1139679e-05	7.5452263e-05	1.3936222e-04	3.5712916e-04	9.2177829e-04	3.5625675e-03	1.7644789e-02	0.0000000e+00	1.6813804e-02	1.9466478e-03	6.3945152e-04	4.4342852e-04	1.1213520e-04	4.3971786e-05	3.3500119e-05	6.91945
10	2.4985113e-05	3.2573899e-05	5.0477411e-05	5.4713314e-05	1.2879299e-04	3.3144914e-04	7.0175316e-04	3.0370397e-03	1.6813804e-02	0.0000000e+00	1.6655841e-02	1.7642280e-03	7.0754954e-04	9.9464903e-05	5.7267839e-05	3.0816854e-05	1.05343
11	2.5590425e-05	1.9319770e-05	2.8254164e-05	5.9581203e-05	5.9500099e-05	1.2702209e-04	1.4779156e-04	3.5304129e-04	1.9466478e-03	1.6655841e-02	0.0000000e+00	1.7645566e-02	1.5709162e-03	4.9523747e-04	1.3432011e-04	3.7420473e-05	1.67419
12	2.8726228e-05	2.3323881e-05	2.3339032e-05	6.3079982e-05	5.2382074e-05	3.8841596e-05	7.8088119e-05	1.8011513e-04	6.3945152e-04	1.7642280e-03	1.7645566e-02	0.0000000e+00	1.4178773e-02	3.2415206e-03	4.5611178e-04	1.0950759e-04	1.62004
13	2.3943201e-05	1.4800031e-05	1.5522269e-05	2.2929513e-05	2.4442247e-05	5.5882908e-05	5.2376972e-05	6.9889380e-05	1.4342852e-04	7.0754954e-04	1.5709162e-03	1.4178773e-02	0.0000000e+00	9.6950001e-03	2.2574454e-03	1.9609617e-04	7.97919
14	1.1500636e-05	1.7111485e-05	1.6889351e-05	1.5111115e-05	1.5047869e-05	2.0551691e-05	3.2497361e-05	4.3712114e-05	1.1213520e-04	9.9464903e-05	4.9523747e-04	3.2415206e-03	9.6950001e-03	0.0000000e+00	1.8337052e-02	2.0605517e-03	7.44265
15	2.0336616e-05	1.0901536e-05	1.5982226e-05	1.4162460e-05	1.3844106e-05	1.5148242e-05	2.4545127e-05	5.1189010e-05	4.3971786e-05	5.7267839e-05	1.3432011e-04	4.5611178e-04	2.2574454e-03	1.8337052e-02	0.0000000e+00	1.0353311e-02	5.79250
16	1.4936018e-05	1.8919890e-05	9.3263652e-06	2.0749348e-05	1.2028788e-05	1.2994719e-05	2.3055756e-05	1.5575146e-05	3.3500119e-05	3.0816854e-05	3.7420473e-05	1.0950759e-04	1.9609617e-04	2.0605517e-03	1.0353311e-02	0.0000000e+00	9.90068
17	1.8355422e-05	1.2735200e-05	1.4899357e-05	1.1038199e-05	1.3227588e-05	1.3969567e-05	1.1644838e-05	6.3467556e-06	6.9194553e-06	1.0534385e-05	1.6741902e-05	1.6200486e-05	7.9791958e-06	7.4426538e-05	5.7925088e-04	9.9806806e-03	0.00000
18	3.2298953e-06	3.3837263e-06	5.3314993e-06	4.7950106e-06	6.3210691e-06	5.8796519e-06	8.3041842e-06	7.7603505e-06	3.1259472e-06	5.2204157e-06	1.5086002e-05	4.7644381e-06	7.1095160e-06	1.0645662e-05	2.4700177e-05	8.2911262e-05	1.86178
19	4.4677560e-06	4.7428383e-06	6.0716440e-06	4.7969815e-06	2.9160544e-06	3.8039563e-06	3.8293651e-06	1.6562121e-05	3.5038938e-06	4.7117878e-06	8.9314510e-06	4.6646346e-06	6.0353538e-06	2.6299824e-05	2.9593053e-05	1.0370181e-05	2.11509
20	8.2462316e-06	7.0966123e-06	4.5734907e-06	4.6477280e-06	9.5999351e-06	3.2526666e-06	8.6831728e-06	4.4820783e-06	2.4838929e-05	6.3545159e-06	9.5611235e-06	2.4502155e-05	7.7220618e-06	1.0682129e-05	6.3531556e-06	3.3440779e-05	1.45087
21	1.0437569e-05	6.9074989e-06	5.6157108e-06	1.4275410e-05	5.8249460e-06	5.5006381e-06	4.5807318e-06	9.3632424e-06	7.8026926e-06	7.1146360e-06	1.1796087e-05	5.5590494e-06	6.6923264e-06	4.1939962e-06	8.1372829e-06	4.9185977e-06	1.21383
22	1.2041979e-05	9.6196860e-06	1.3010478e-05	9.4053617e-06	5.0436477e-06	7.7167635e-06	8.5694078e-06	9.9286129e-06	5.7376271e-06	6.3776029e-06	8.6329767e-06	4.9544570e-06	4.8546440e-06	5.6792254e-06	1.1142403e-05	6.9313828e-06	4.83116
23	6.6486917e-06	8.4153127e-06	8.5363196e-06	1.2279626e-05	4.8089207e-06	5.4330684e-06	7.2972302e-06	4.1025846e-06	5.4281487e-06	4.3455844e-06	7.2439852e-06	3.7812074e-06	9.0391738e-06	9.0771757e-06	1.2425641e-05	1.0977574e-05	1.13493
24	6.2444242e-06	6.1438612e-06	4.8601486e-06	5.8792543e-06	8.7675542e-06	7.2138141e-06	8.2907925e-06	5.7327490e-06	5.7830940e-06	4.1105534e-06	2.3369909e-06	1.3873216e-05	6.2174945e-06	4.0423666e-06	7.1696503e-06	5.3460776e-06	6.80044
25	5.8655972e-06	7.6321509e-06	3.5362899e-06	2.9675077e-06	6.1433077e-06	4.7846250e-06	5.6282712e-06	3.9570541e-06	5.8765002e-06	4.2376607e-06	2.4747004e-06	4.5219428e-06	5.1167607e-06	5.5696672e-06	6.2923685e-06	1.4057049e-05	7.09033
26	4.2638600e-06	5.3072463e-06	4.5425800e-06	3.2688449e-06	4.0502466e-06	5.7834839e-06	4.1486221e-06	4.1876792e-06	5.5460662e-06	4.7365759e-06	3.6282032e-06	2.6773280e-06	5.9176402e-06	3.1758993e-06	3.6883302e-06	1.8678232e-06	2.39513
27	8.8550551e-06	7.1359614e-06	3.4555545e-06	2.3442013e-06	4.1691096e-06	8.0756651e-06	5.4315242e-06	5.1614649e-06	4.2423411e-06	2.8180069e-06	2.2910271e-06	2.0737794e-06	4.1599838e-06	3.1457380e-06	8.0178924e-06	3.0141975e-06	2.82899
28	3.7216413e-06	4.0017092e-06	4.8947105e-06	8.6433261e-06	4.8089567e-06	9.9205230e-06	3.9077485e-06	5.2151791e-06	2.4806611e-06	1.6118636e-06	2.2402420e-06	2.3801660e-06	2.6849503e-06	3.6147178e-06	2.6485344e-06	3.5365755e-06	2.68217
29	2.3733644e-06	4.4830157e-06	7.4330115e-06	6.8677059e-06	4.7865868e-06	7.2694588e-06	4.1318070e-06	7.5696361e-06	2.4970313e-06	2.4141940e-06	3.1115108e-06	2.2756155e-06	7.6580749e-06	3.0072074e-06	8.9901208e-06	3.1481263e-06	2.74901
30	5.2607595e-06	4.9522101e-06	2.4210290e-06	3.9605548e-06	7.6374119e-06	4.4642042e-06	3.8577742e-06	3.9894017e-06	2.0662540e-06	2.8244032e-06	4.2893659e-06	4.2852656e-06	5.1667322e-06	2.6016186e-06	4.4989107e-06	8.7567880e-06	4.14287
31	1.1004788e-05	3.5213165e-06	3.3336056e-06	3.4917105e-06	3.4010647e-06	3.4371825e-06	3.4131527e-06	2.5402854e-06	1.8784828e-06	3.0604669e-06	2.8334684e-06	2.4689837e-06	1.0267647e-06	8.1942257e-07	9.5625556e-07	1.9814544e-06	1.16817
32	2.4526254e-06	1.8330024e-06	8.0735540e-07	2.1547473e-06	1.1055084e-06	1.0886963e-06	9.5625739e-07	1.4893742e-06	9.8760335e-07	1.7520177e-06	9.8588018e-07	2.5557047e-06	1.7887063e-06	5.5523874e-06	2.0615102e-06	1.4255467e-06	1.32474
33	4.1312634e-06	3.7836707e-06	3.7288820e-06	1.2726375e-06	1.6554981e-06	1.7676114e-06	1.6546501e-06	2.7037644e-06	1.7136732e-06	1.7091996e-06	2.8347228e-06	2.1007845e-06	1.0932227e-06	2.0559247e-06	3.8236904e-06	2.9255554e-06	1.78130
34	5.2606701e-06	3.6894083e-06	3.9935121e-06	3.7767706e-06	2.7296826e-06	2.9799842e-06	5.9391734e-06	3.4332561e-06	1.9638260e-06	1.4645848e-06	1.2766468e-06	3.4574681e-06	1.6892038e-06	1.1581114e-06	9.0345370e-07	8.8841049e-07	1.11783
35	5.5433301e-06	2.6948357e-06	3.6930593e-06	2.8396574e-06	3.5814943e-06	5.5507881e-06	2.8165173e-06	1.3645706e-06	2.3281400e-06	2.1663512e-06	1.3099869e-06	1.5376522e-06	1.3891328e-06	9.8514465e-07	7.9597167e-07	7.6055115e-07	9.94151
36	3.9822667e-06	4.0474666e-06	4.3534094e-06	3.3897179e-06	4.6429685e-06	3.0015796e-06	2.4399192e-06	2.1371322e-06	2.5442887e-06	1.9416210e-06	9.9496841e-07	2.0668346e-06	1.0037794e-06	1.4840578e-06	9.6541274e-07	1.1044559e-06	9.28813
37	6.0509529e-06	2.9431779e-06	4.4509730e-06	2.5373509e-06	3.1746024e-06	2.7106490e-06	3.8175576e-06	2.9391917e-06	2.6938691e-06	1.7387484e-06	1.6580630e-06	1.2296419e-06	1.5371218e-06	1.9717113e-06	1.2487567e-06	2.0845867e-06	2.91860
38	5.5440907e-06	4.0229628e-06	2.7800952e-06	4.8192063e-06	2.9400997e-06	4.1792995e-06	3.2692673e-06	1.3488216e-06	2.6124515e-06	2.1650132e-06	1.6266741e-06	2.8571252e-06	1.9641469e-06	1.2283768e-06	2.0086266e-06	1.7421672e-06	2.84742
39	2.5028504e-06	3.6866359e-06	2.5479294e-06	2.6898758e-06	4.5017947e-06	5.5740560e-06	2.9564657e-06	1.9830949e-06	2.2993907e-06	2.0318383e-06	2.2216657e-06	7.7395876e-06	1.4976571e-06	1.7170732e-06	8.8911119e-07	2.0757859e-06	3.77891
40	3.3624419e-06	5.4824814e-06	4.3630264e-06	3.7032419e-06	5.3702773e-06	3.9013021e-06	3.8710977e-06	1.6467540e-06	3.2744394e-06	4.5455157e-06	2.4048927e-06	2.4016753e-06	2.1147050e-06	2.6635314e-06	2.1049245e-06	3.1828227e-06	2.84663
41	2.7352949e-06	2.8348221e-06	2.0532460e-06	3.4636675e-06	1.6731610e-06	1.5472611e-06	1.1584962e-06	5.1597588e-07	1.1345158e-06	2.4651255e-06	1.8160671e-06	1.8076387e-06	1.1683065e-06	1.2460403e-06	7.2958359e-07	2.0664150e-06	4.04523
42	1.2333056e-06	3.0410433e-06	1.3117947e-06	1.7923143e-06	1.1723447e-06	1.4832220e-06	2.3358352e-06	1.0972021e-06	2.3069507e-06	8.8542179e-06	1.9017690e-06	2.9220069e-06	2.5849777e-06	1.5993322e-06	2.1759523e-06	4.5131452e-06	3.18996
43	1.2173009e-06	1.0310309e-06	6.3964220e-07	1.2138001e-06	9.5419652e-07	9.7554398e-07	5.6925005e-07	4.7279647e-07	4.6103209e-07	6.4091755e-07	7.1171428e-07	8.4930714e-07	1.2366176e-06	7.5993383e-07	1.0779022e-06	6.7219369e-07	9.21715
44	1.1749021e-06	9.8180676e-07	7.0769095e-07	6.5598207e-07	6.8931073e-07	1.0517704e-06	9.2513764e-07	8.5580727e-07	4.6012262e-07	5.7707556e-07	7.4049218e-07	7.7258634e-07	8.1250371e-07	8.8372864e-07	7.0814422e-07	5.3534779e-07	6.35493
45	3.2350187e-06	1.5481799e-06	1.6638394e-06	1.9935384e-06	1.4202902e-06	2.3514577e-06	7.0333702e-07	6.3478609e-07	9.1361415e-07	8.7065270e-07	6.9838110e-07	1.2407161e-06	7.4554183e-07	3.9668918e-07	4.1883227e-07	4.0336562e-07	6.59115
46	1.3377494e-06	7.9082237e-07	8.0116776e-07	6.6089755e-07	1.1506988e-06	8.9790858e-07	1.0841445e-06	4.1182299e-07	1.3347679e-06	1.0172914e-06	6.3164014e-07	5.3387807e-07	8.5275594e-07	4.9736866e-07	3.1041897e-07	2.3678986e-06	3.10471
47	1.8999119e-06	9.9184933e-07	1.2483672e-06	1.8000610e-06	8.8842196e-07	1.2562670e-06	1.1269543e-06	1.2062269e-06	1.6258058e-06	1.5413091e-06	4.3587023e-07	4.7234366e-07	5.2098122e-07	2.8007545e-07	2.6902716e-07	9.3661960e-07	4.87732
48	1.9125094e-06	1.5811519e-06	1.5333980e-06	1.4220572e-06	1.2308510e-06	9.3548015e-07	5.8352537e-07	1.3327553e-06	5.6815964e-07	7.5748253e-07	4.3442186e-07	5.7542954e-07	2.6789353e-07	2.9427155e-07	1.8814532e-07	1.4779179e-06	5.89282
49	1.8746552e-06	1.1516591e-06	5.2841670e-07	6.7575739e-07	8.6748241e-07	1.1335755e-06	6.2093241e-07	6.3020083e-07	4.8054355e-07	6.4184322e-07	1.0586867e-06	5.8236285e-07	6.0512279e-07	1.0288226e-06	1.0886182e-06	8.0311720e-07	6.77082
50	8.5229696e-07	1.0030036e-06	6.8073697e-07	1.0813925e-06	1.0981303e-06	1.3061471e-06	9.2051733e-07	5.6557985e-07	6.2266543e-07	6.8610185e-07	5.1925128e-07	5.2252371e-07	7.6126514e-07	1.4578146e-06	3.2815783e-06	1.1197581e-06	6.35004
51	1.4668819e-06	1.1100113e-06	1.2631989e-06	7.5186929e-07	7.9707067e-07	8.2130454e-07	1.1892857e-06	1.0913771e-06	7.2925823e-07	6.3135789e-07	4.7812733e-07	4.6643108e-07	3.6240356e-07	2.3896330e-07	8.2289348e-07	4.5866562e-07	4.89972
52	1.4096403e-06	1.3291827e-06	1.1657602e-06	8.9984910e-07	1.0534283e-06	9.8354071e-07	1.0986788e-06	4.8304442e-07	7.2137180e-07	5.3015295e-07	6.0790708e-07	7.3087791e-07	3.7947407e-07	4.9901117e-07	8.2462941e-07	2.6067778e-07	2.78174
53	1.1443800e-06	5.3776552e-07	9.8214130e-07	1.2883245e-06	5.4878639e-07	5.8718623e-07	6.4098619e-07	2.4107301e-07	4.9858834e-07	6.1296692e-07	5.8402541e-07	4.7321667e-07	6.4020075e-07	4.5005659e-07	5.8305603e-07	5.6836328e-07	6.05704
54	8.3399054e-07	1.1208474e-06	1.1165150e-06	5.5773510e-07	7.2845778e-07	8.4789817e-07	7.4529889e-07	9.4854892e-07	7.6589017e-07	4.5579103e-07	5.6386356e-07	9.3011346e-07	5.4823628e-07	6.3035343e-07	5.2558276e-07	7.4789808e-07	1.76779
55	8.4740872e-07	6.8187527e-07	1.1669427e-06	8.7845654e-07	2.5993985e-06	4.2247994e-06	5.9904405e-07	8.4203322e-07	5.9171979e-07	8.4590337e-07	8.6236845e-07	8.5437509e-07	6.0417544e-07	3.9324946e-07	3.7073099e-07	5.8310776e-07	7.68448
56	7.1885251e-07	5.3517065e-07	1.5225858e-06	9.3005811e-07	8.2336455e-07	1.1728003e-06	1.7800697e-06	8.3047299e-07	1.2697011e-06	1.1354884e-06	4.6923687e-07	7.3753606e-07	1.2582262e-06	1.3081041e-06	1.3095383e-06	9.7865302e-07	5.46277
57	6.4792231e-07	1.2218200e-06	1.7095059e-06	1.2653702e-06	1.6336623e-06	2.3321939e-06	1.4117215e-06	1.0779804e-06	1.0571071e-06	6.7893892e-07	5.2796687e-07	3.7551029e-07	5.8390029e-07	4.5558178e-07	5.9701340e-07	1.6902718e-06	8.16540
58	2.1327880e-06	1.2341347e-06	2.3402215e-06	1.3390101e-06	1.0045948e-06	1.2371838e-06	1.1809702e-06	5.3757010e-07	8.8193482e-07	5.5559816e-07	2.2893671e-07	5.5359376e-07	4.4953251e-07	7.2817123e-07	1.3423110e-06	1.0323020e-06	7.31724
59	6.9919447e-07	1.2636428e-06	1.1575564e-06	1.8387838e-06	1.8601720e-06	1.0829121e-06	1.9175191e-06	1.1273849e-06	7.9515444e-07	5.8332858e-07	6.9887899e-07	8.0599400e-07	6.5398672e-07	1.0793517e-06	6.5656148e-07	1.4907351e-06	8.79020
60	5.5119092e-07	8.9088149e-07	1.0283403e-06	1.5353262e-06	1.7714651e-06	1.2824077e-06	1.1578517e-06	1.0757897e-06	6.9809324e-07	8.3082812e-07	1.3493808e-06	8.8492706e-07	8.8338241e-07	8.3881388e-07	8.0126041e-07	6.2545913e-07	4.48312
61	4.8826593e-07	5.5942828e-07	4.5296960e-07	7.5088076e-07	1.2871337e-06	1.0945624e-06	1.3749244e-06	1.1290067e-06	1.0541707e-06	9.6269887e-07	1.6504246e-06	1.5302871e-06	8.6205062e-07	1.2019271e-06	1.8833075e-06	7.0686598e-07	1.05658

Nonadiabatic couplings without spin

- **Code will produce the Redfield tensor elements and correlation function:**





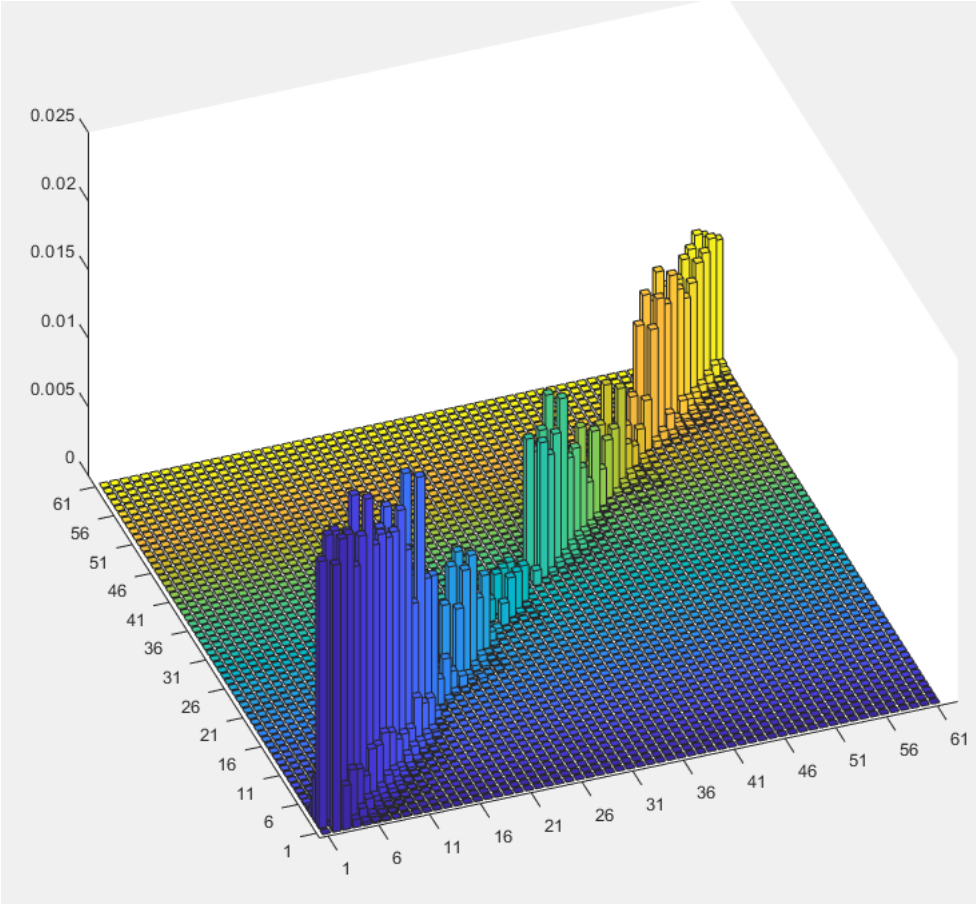
❖ Maximal transition probability appears near main diagonal.

❖ Almost zero transition probability when get away from the main diagonal

❖ Quite small at HOMO to LUMO transition.

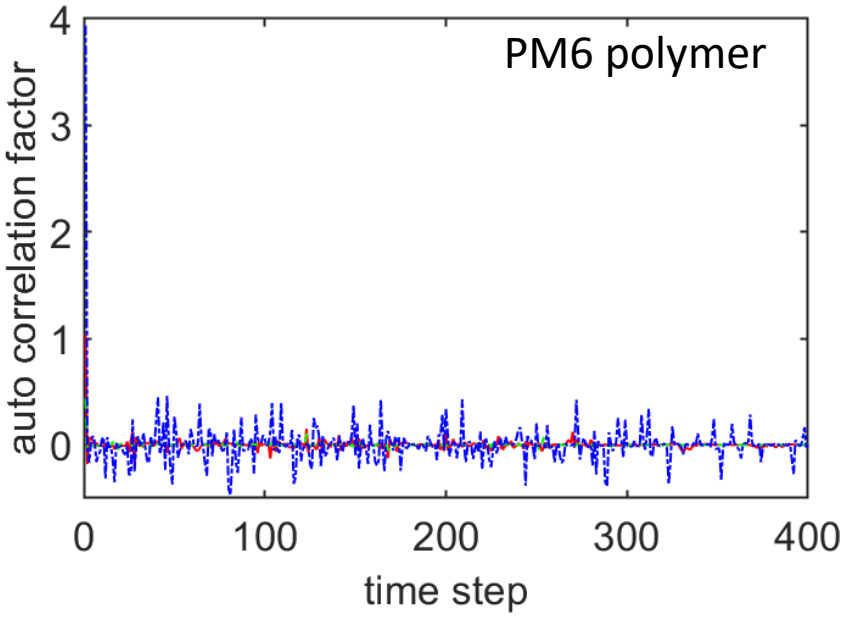
Nonadiabatic couplings without spin

- **Redfield tensor elements for PM6 polymer:**



Nonadiabatic couplings without spin

- **Code will produce the Redfield tensor elements and correlation function:**



- Auto correlation function should decay from 1 to 0 in a certain time steps and then oscillate around 0.
- The fast decay of the correlation function justifies use of shorter trajectory.

Redfield MATLAB Script Parameters

Tuesday June 21, 2022

Adam Flesche

Required Input Files

- RRR (main output from correlation script)
- energy_pop (used in correlation script)
- Red_FIELD_MEq_11d_emi6_1f.m (MATLAB Redfield script in ~/bin/)
- **forMasterOptics**
- **bandout**

forMasterOptics

- Syntax used in the script, initially generated as “forMasterEq” in your geometry optimization directory:

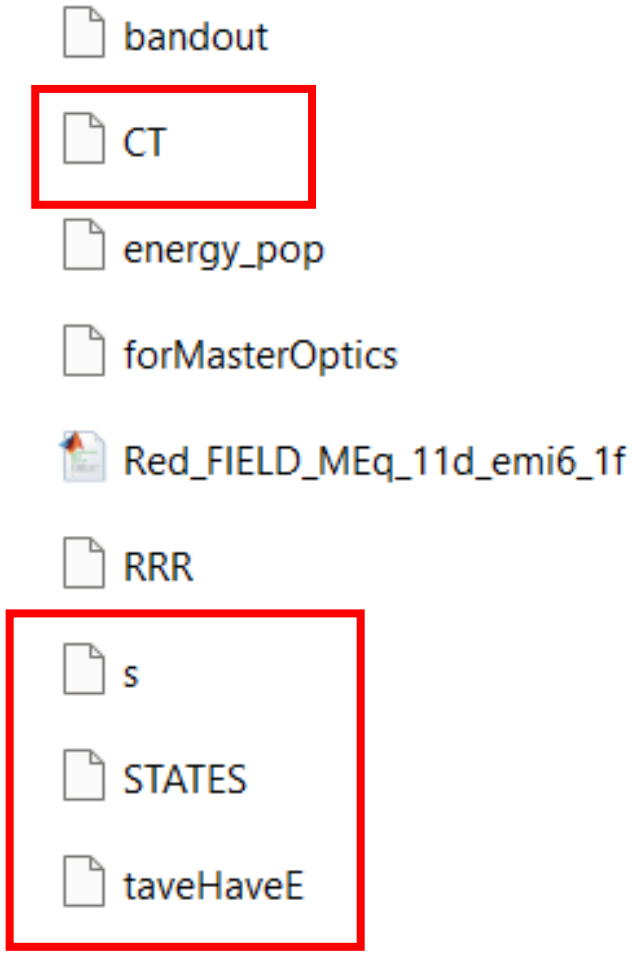
- Edit input_overlap to contain your desired orbital interval
- Run a script: ~/bin/OS/OS_dipol_v3b
- Obtains forMasterEQ file
- Simply cp forMasterEQ forMasterOptics

bandout

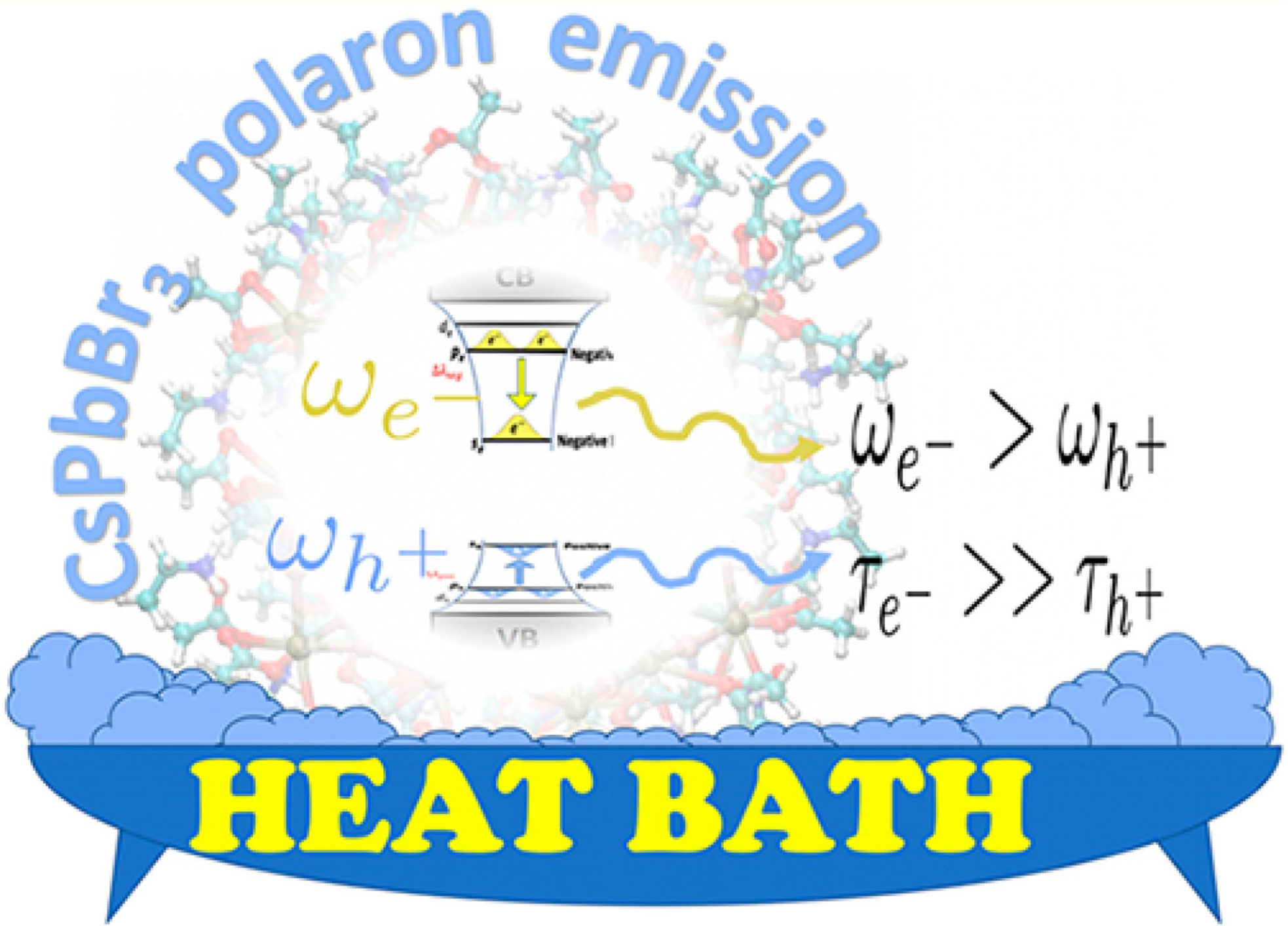
- Requires you to run a VASP job to obtain partial charge densities, PARCHG files
- Job run with INCAR-pc and CONTCAR from optimization
- When finished, run the integration script:
- cp ~/bin/band_integrate_vasp5.pl
- Edit to fit your orbital interval
- Run with perl band_integrate_vasp5.pl
- bandout is obtained as the output

MATLAB Output Files

- CT
- s
- STATES
- taveHaveE



Questions?


polaron emission
$CsPbBr_3$
CB
VB
ω_{e^-}
ω_{h^+}
$\omega_{e^-} > \omega_{h^+}$
$\tau_{e^-} >> \tau_{h^+}$
HEAT BATH

Unitary evolution,
without dissipation

$$i\hbar\frac{\partial\rho}{\partial t} = [H,\rho]$$

$$\rho(t) = e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}$$

concept of thermal bath

$$\boldsymbol{\rho}^{world} = \boldsymbol{\rho}^{system} \otimes \boldsymbol{\rho}^{BATH}$$

dissipative evolution

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[H,\rho] - \frac{1}{\hbar^2}tr\left(\boldsymbol{\rho}^{BATH}\int d\tau\ \left[V(t),\left[V(t+\tau),\rho(t)\right]\right]\right)$$

short-hand form

$$\frac{\partial}{\partial t}\rho = (\hat{L}+\hat{R})\rho$$

system of first order differential equations
for elements $\boldsymbol{\rho_{ij}}$

matrix elements
of density operator

$$\rho = \sum_j \boldsymbol{\rho_{ij}}|\psi_i\rangle\langle\psi_j|$$

eigenvalue problem

$$(\hat{L}+\hat{R})\rho^{(\xi)} = \Omega^{(\xi)}\rho^{(\xi)}$$

$$\boldsymbol{\rho_{ij}}(t) = \sum_\xi \left\langle \rho_{ij}^{(a,b)}(0)\middle|\rho^{(\xi)}\right\rangle \rho^{(\xi)}\exp(\Omega^{(\xi)}t)$$

solution:
time evolution of
matrix element
of density
operator

initial excitation
from orbital a to orbital b

eigenvalues
(rates of dissipation)

$$\boldsymbol{\rho_{ij}}(t) = \sum_{\xi} \left\langle \rho_{ij}^{(a,b)}(0) \middle| \rho^{(\xi)} \right\rangle \rho^{(\xi)} \exp(\Omega^{(\xi)} t)$$

time

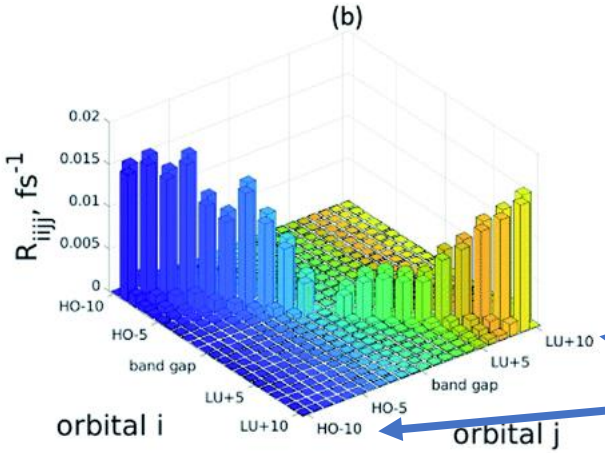
initial condition
at time t=0

expansion
coefficients

eigenvectors
of density matrix

Input Parameters

of pXXX files




```
timeSTEPS=600;

iH=2;%12;%22;%31;%3;
%initial ho
iE=2;%8;%2;%4;%3;%5;
%initial electron
HOMO=82
LUMO=HOMO+1
Omin=64
Omax=99
KKKmax=Omax-Omin+1;
```

Re

17x17 double

	1	2	3	4	5	6	7	8	9	10	11	
1	0	0.0192	0.0251	4.5893e-...	0.0015	3.0673e-...	2.7195e-...	2.4123e-...	1.2798e-...	2.4502e-...	3.3432e-...	1.9
2	0	-0.0476	0.0034	0.0127	9.1686e-...	8.0528e-...	3.4390e-...	4.7586e-...	3.4791e-...	1.8069e-...	3.7412e-...	3.2
3	0	0	-0.0197	0.0076	0.0053	0.0010	8.8460e-...	7.3312e-...	6.3325e-...	6.1950e-...	9.1909e-...	5.2
4	0	0	0	-0.0171	0.0090	0.0035	0.0013	0.0013	0.0011	1.5954e-...	1.2986e-...	1.7
5	0	0	0	0	-0.0190	0.0046	0.0078	0.0058	0.0034	2.9284e-...	2.6625e-...	1.5
6	0	0	0	0	0	-0.0241	0.0128	0.0092	0.0071	5.0792e-...	7.2989e-...	9.2
7	0	0	0	0	0	0	-0.0389	4.0941	0.2139	0.0049	0.0083	
8	0	0	0	0	0	0	0	-4.3546	3.1692	0.0118	0.0130	
9	0	0	0	0	0	0	0	0	3.2581	0.0368	0.0183	
10	0	0	0	0	0	0	0	0	0	0.1874	11.6590	
11	0	0	0	0	0	0	0	0	0	0	-12.2729	
12	0	0	0	0	0	0	0	0	0	0	0	-
13	0	0	0	0	0	0	0	0	0	0	0	
14	0	0	0	0	0	0	0	0	0	0	0	
15	0	0	0	0	0	0	0	0	0	0	0	
16	0	0	0	0	0	0	0	0	0	0	0	
17	0	0	0	0	0	0	0	0	0	0	0	
18												

Rh

19x19 double

	1	2	3	4	5	6	7	8	9	10	11	
1	-0.0181	0.0025	0.0099	7.5284e-...	9.8307e-...	3.4980e-...	4.8575e-...	7.5899e-...	1.7284e-...	1.1368e-...	9.8725e-...	3.3
2	0	-0.0193	0.0087	0.0041	0.0010	6.9581e-...	1.6402e-...	4.3801e-...	3.5001e-...	6.3856e-...	4.9990e-...	1.0
3	0	0	-0.0221	0.0103	0.0031	4.3922e-...	0.0012	1.5939e-...	3.4960e-...	2.7536e-...	2.0108e-...	6.5
4	0	0	0	-0.0218	0.0041	0.0088	5.7140e-...	0.0019	5.3630e-...	0.0011	0.0010	2.8
5	0	0	0	0	-0.0558	0.0043	0.0037	0.0012	0.0022	0.0010	8.6223e-...	
6	0	0	0	0	0	-2.3920	0.0062	0.0105	0.0073	0.0150	0.0080	
7	0	0	0	0	0	0	-4.1256	2.2827	0.0481	0.0302	0.0054	
8	0	0	0	0	0	0	0	-6.2401	3.3715	0.3981	0.2976	
9	0	0	0	0	0	0	0	0	-4.8304	5.9407	0.1448	
10	0	0	0	0	0	0	0	0	0	-4.2262	4.6785	
11	0	0	0	0	0	0	0	0	0	0	-3.9637	
12	0	0	0	0	0	0	0	0	0	0	0	
13	0	0	0	0	0	0	0	0	0	0	0	
14	0	0	0	0	0	0	0	0	0	0	0	
15	0	0	0	0	0	0	0	0	0	0	0	
16	0	0	0	0	0	0	0	0	0	0	0	
17	0	0	0	0	0	0	0	0	0	0	0	
18	0	0	0	0	0	0	0	0	0	0	0	

Redfield Tensor for electrons

```
Efermi=energy_pop(HOMO-Omin+1)/2+energy_pop(LUMO-Omin+1)/2;
Ee=energy_pop(HOMO-Omin+2:Omax-Omin+1)-Efermi;
Eh=Efermi-energy_pop(1:HOMO+1-Omin);
Re=forME(HOMO-Omin+2:Omax-Omin+1,HOMO-Omin+2:Omax-Omin+1);
Rh=forME(1:HOMO+1-Omin,1:HOMO+1-Omin);
Optic=forME(1:HOMO+1-Omin,HOMO-Omin+2:Omax-Omin+1);
```

```
%enhance hole transitions up in energy, disable thermal excitations
for i=1:1; for j=1:HOMO+1-Omin;if Eh(i)>Eh(j) Rh(i,j)=0; end;end;end;

for i=2:HOMO+1-Omin;
for j=1:HOMO+1-Omin;
%    if Eh(i)>Eh(j) Rh(i,j)=-Rh(i,j)*(exp( -(Eh(i)-Eh(j))/kT)); end;
    if Eh(i)>Eh(j) Rh(i,j)=0; end;
    %Rh(i,j)=Rh(i,j)*(exp( -(Eh(i)-Eh(j))/kT)   -1).^(-1);
Rh(i,i)=0;
    Gh(i-1)=Gh(i-1)-Rh(i,j);
%    Rh(i,i)=Gh(i);
end;
end;
```

```
%refine master equation coefficients
for i=1:Omax-HOMO;Re(i,i)=Ge(i);end;
for i=1:HOMO+1-Omin;Rh(i,i)=Gh(i);end;
```

Redfield Tensor for holes

U

19x19 double

	1	2	3	4	5	6	7	8	9	10	11	
1	1	-0.9005	-0.1716	-0.1009	-0.0094	-1.4443e...	-1.1699e...	4.8801e-...	8.6232e-...	1.1223e-...	-1.2474e...	-1.
2	0	0.4348	-0.9378	-0.9563	-0.0016	-2.8554e...	-3.8359e...	-2.8570e...	-3.5570e...	3.0491e-...	-5.2449e...	-2.
3	0	0	0.3016	0.2744	-0.0530	-1.6687e...	-2.9025e...	1.2389e-...	2.1735e-...	2.7915e-...	-3.0820e...	-4.
4	0	0	0	0.0072	-0.1202	-0.0037	-1.3062e...	-1.3472e...	-1.4918e...	1.0542e-...	-1.7400e...	-4.
5	0	0	0	0	0.9913	-0.0018	-9.1647e...	3.1832e-...	6.1783e-...	8.6764e-...	-9.9818e...	
6	0	0	0	0	0	1.0000	-0.0036	-6.6575e...	8.1610e-...	0.0030	-0.0047	
7	0	0	0	0	0	0	1.0000	-0.7336	-0.9491	-0.9987	0.9965	
8	0	0	0	0	0	0	0	0.6796	0.2905	0.0435	0.0696	
9	0	0	0	0	0	0	0	0	0.1215	0.0256	0.0462	
10	0	0	0	0	0	0	0	0	0	0.0026	0.0067	
11	0	0	0	0	0	0	0	0	0	0	3.7740e-...	
12	0	0	0	0	0	0	0	0	0	0	0	
13	0	0	0	0	0	0	0	0	0	0	0	
14	0	0	0	0	0	0	0	0	0	0	0	
15	0	0	0	0	0	0	0	0	0	0	0	
16	0	0	0	0	0	0	0	0	0	0	0	
17	0	0	0	0	0	0	0	0	0	0	0	
18	0	0	0	0	0	0	0	0	0	0	0	

eigenvectors

$$Re * U = U * D$$

D

19x19 double

	1	2	3	4	5	6	7	8	9	10	11
1	-0.0181	0	0	0	0	0	0	0	0	0	0
2	0	-0.0193	0	0	0	0	0	0	0	0	0
3	0	0	-0.0221	0	0	0	0	0	0	0	0
4	0	0	0	-0.0218	0	0	0	0	0	0	0
5	0	0	0	0	-0.0558	0	0	0	0	0	0
6	0	0	0	0	0	-2.3920	0	0	0	0	0
7	0	0	0	0	0	0	-4.1256	0	0	0	0
8	0	0	0	0	0	0	0	-6.2401	0	0	0
9	0	0	0	0	0	0	0	0	-4.8304	0	0
10	0	0	0	0	0	0	0	0	0	-4.2262	0
11	0	0	0	0	0	0	0	0	0	0	-3.9637
12	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0

eigenvalues

```
%standard diagonalization
[U,D]=eig(Re);

c=U\psi0;


FREQ=real(diag(D));

psi=c(1)*U*[1  zeros(1,Kmax-1)]'*exp(D(1,1)*t);
```

$$\rho_{ij}(t) = \sum_{\xi} \left\langle \rho_{ij}^{(a,b)}(0) \middle| \rho^{(\xi)} \right\rangle \rho^{(\xi)} \exp(\Omega^{(\xi)} t)$$

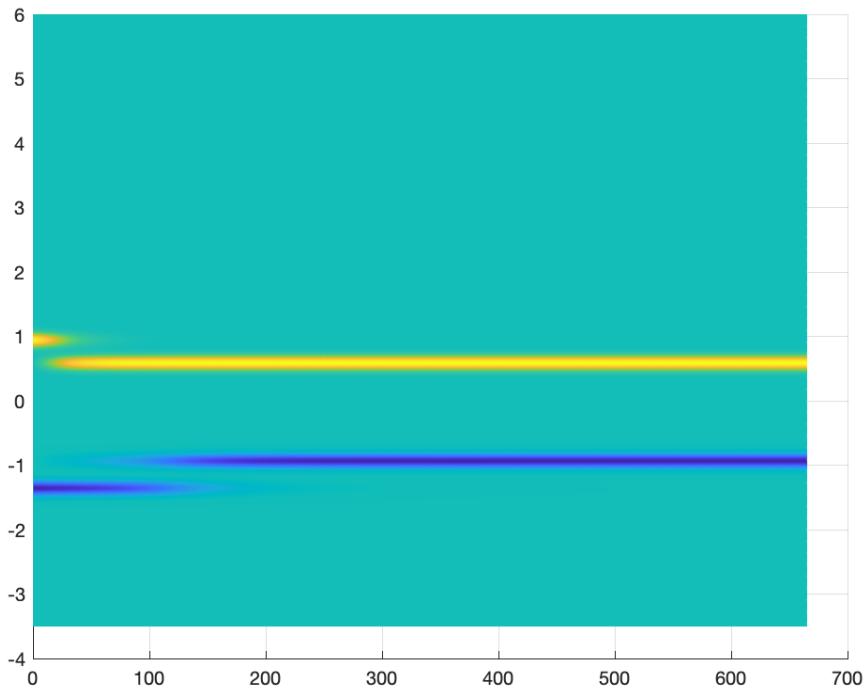
$$\left(\hat{L} + \hat{R}\right)\rho^{\nu} = \Omega\rho^{\nu}$$

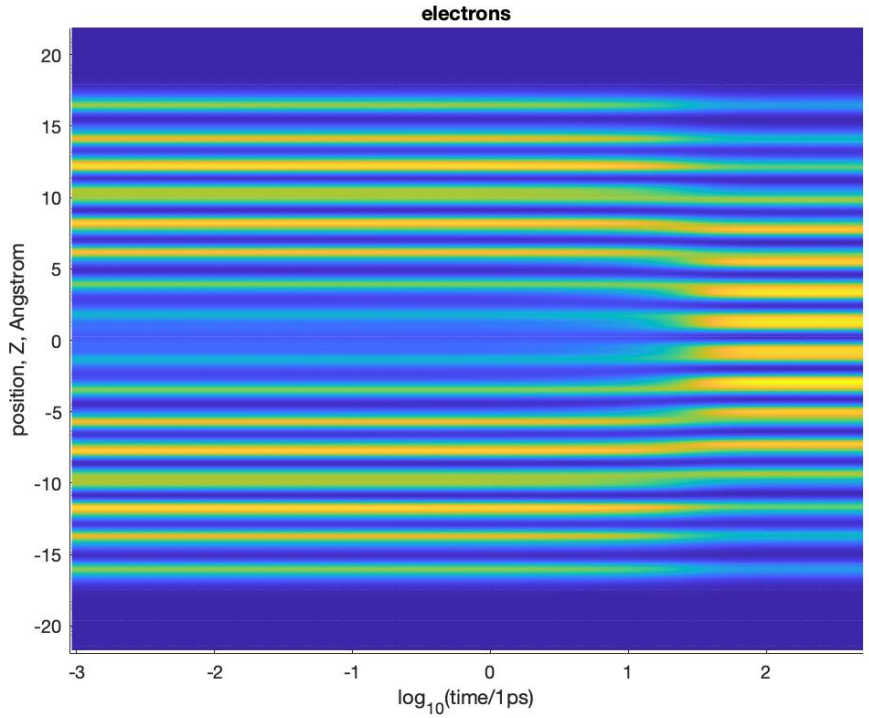
$$\rho_{\sigma,ij}(t) = \sum_{\xi} \left\langle \rho_{\sigma,ij}^{(a,b)}(0) \middle| \rho_{\sigma}^{(\xi)} \right\rangle \rho_{\sigma}^{(\xi)} \exp(\Omega_{\sigma}^{(\xi)} t)$$

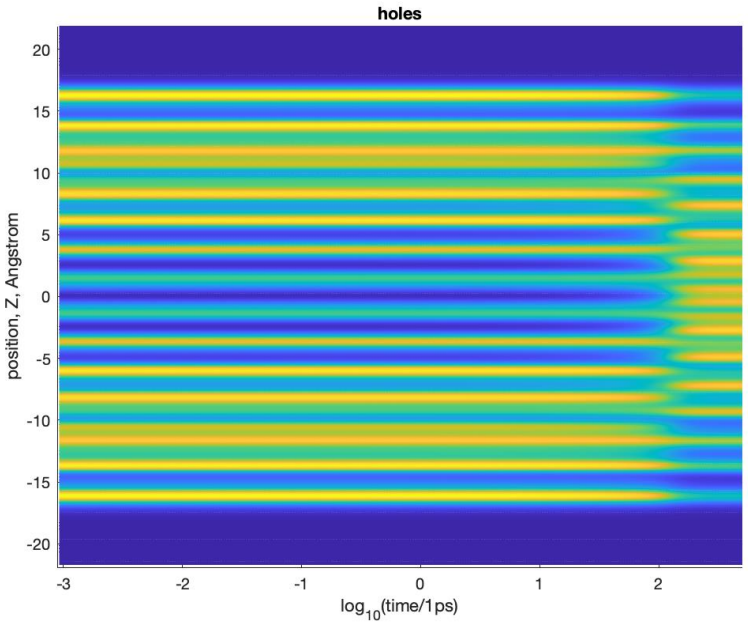
$$\rho = \sum_{j} p_j |\psi_j\rangle\langle\psi_j|$$

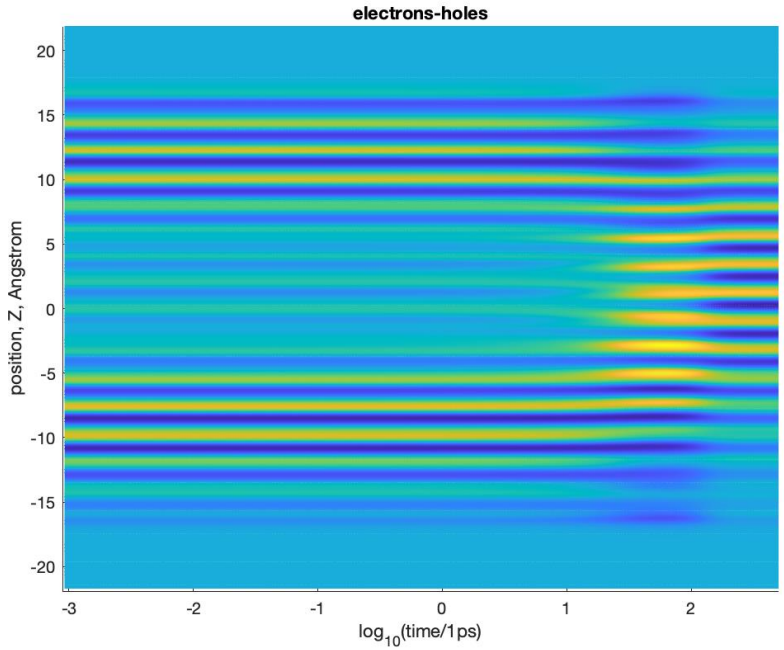
$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]$$

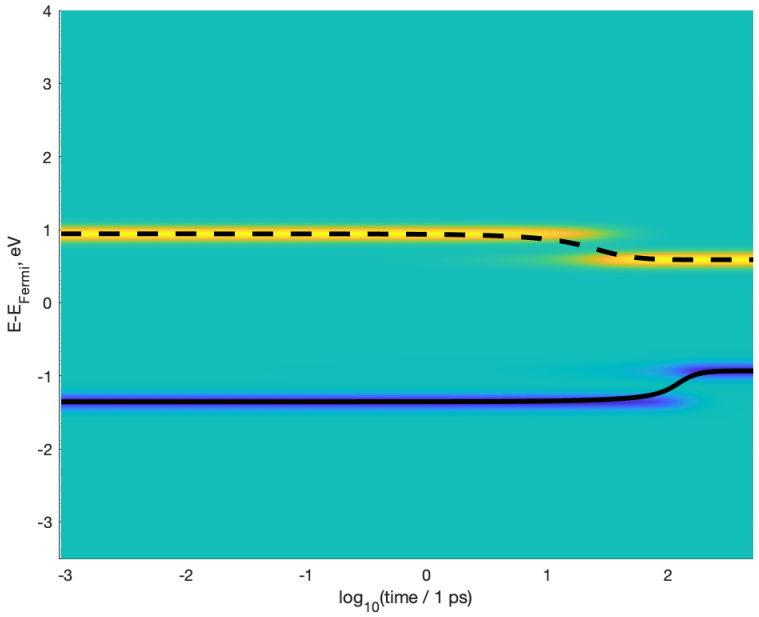
$$\rho(t) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}$$

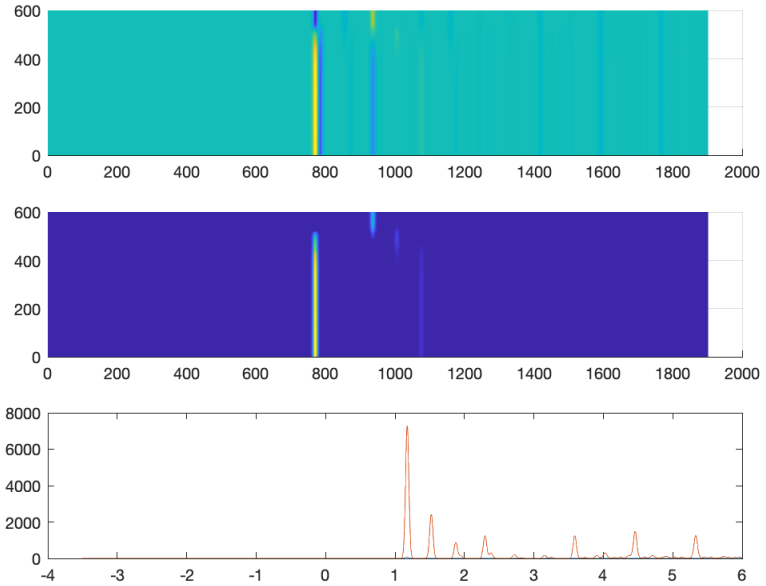

6
5
4
3
2
1
0
-1
-2
-3
-4
0
100
200
300
400
500
600
700

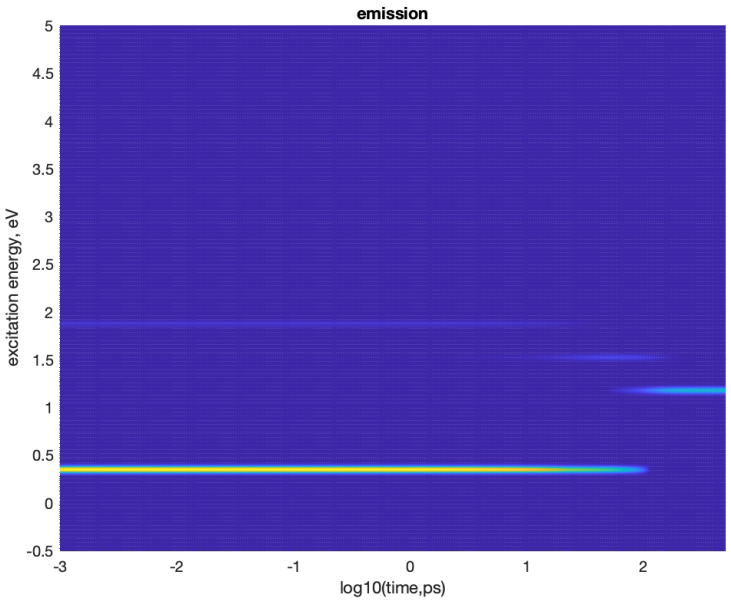

electrons
position, Z, Angstrom
20
15
10
5
0
-5
-10
-15
-20
-3
-2
-1
0
1
2
log10(time/1ps)

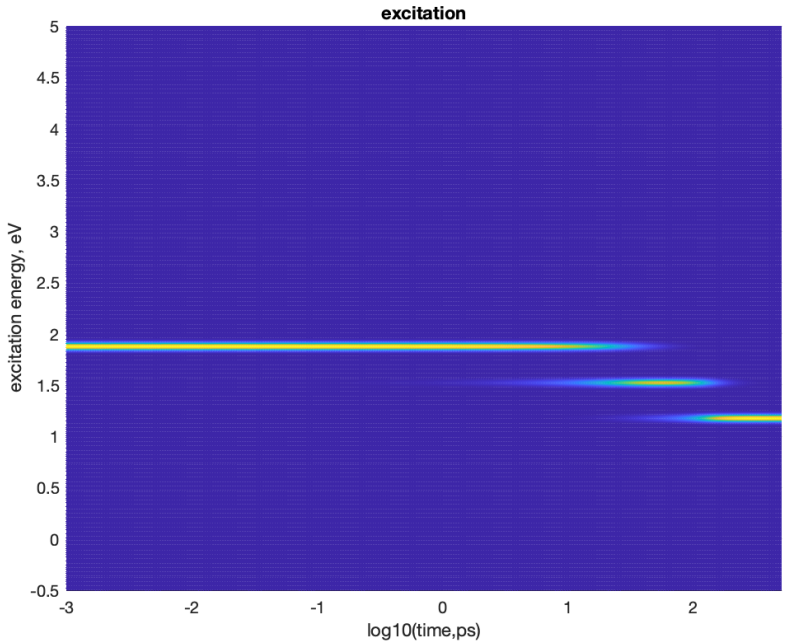

holes
position, Z, Angstrom
20
15
10
5
0
-5
-10
-15
-20
-3
-2
-1
0
1
2
log10(time/1ps)

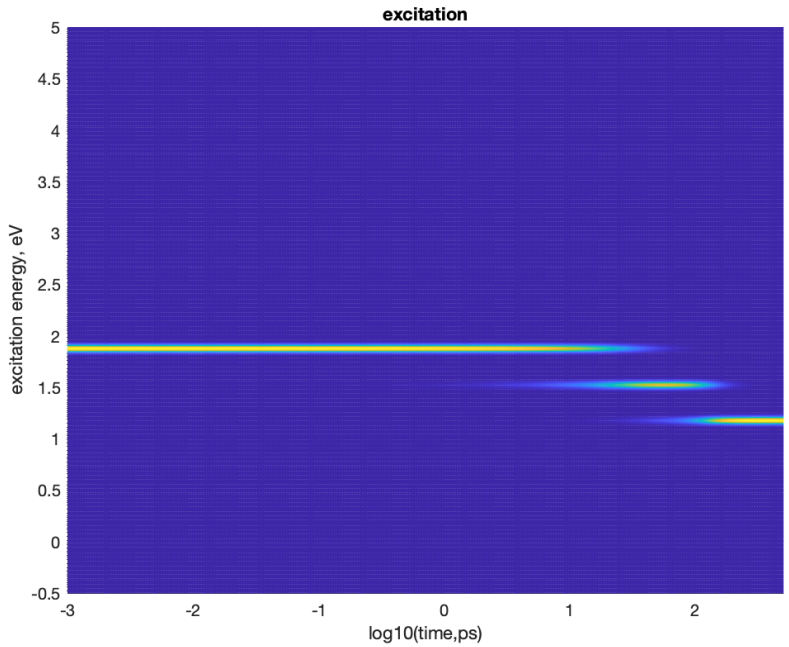

electrons-holes
position, Z, Angstrom
20
15
10
5
0
-5
-10
-15
-20
-3
-2
-1
0
1
2
log10(time/1ps)

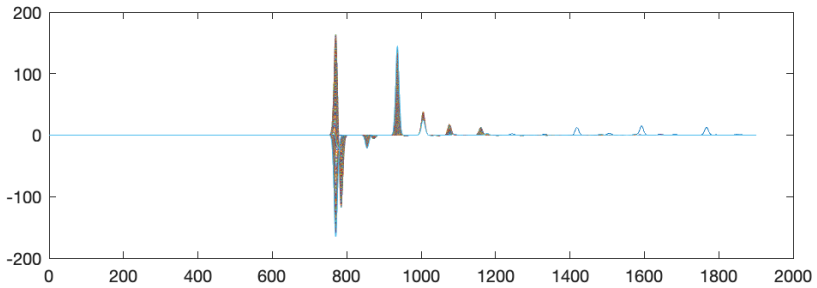

E-E_Fermi, eV
log10(time / 1 ps)

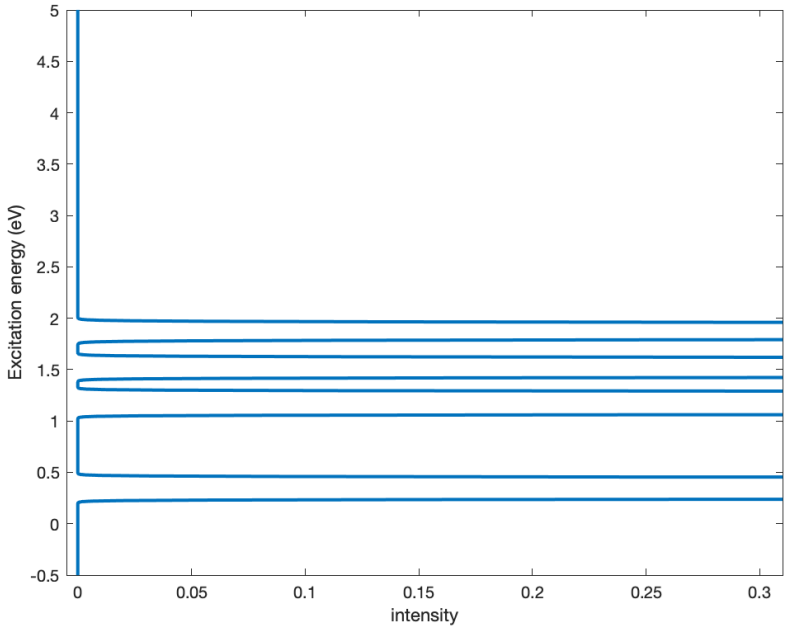


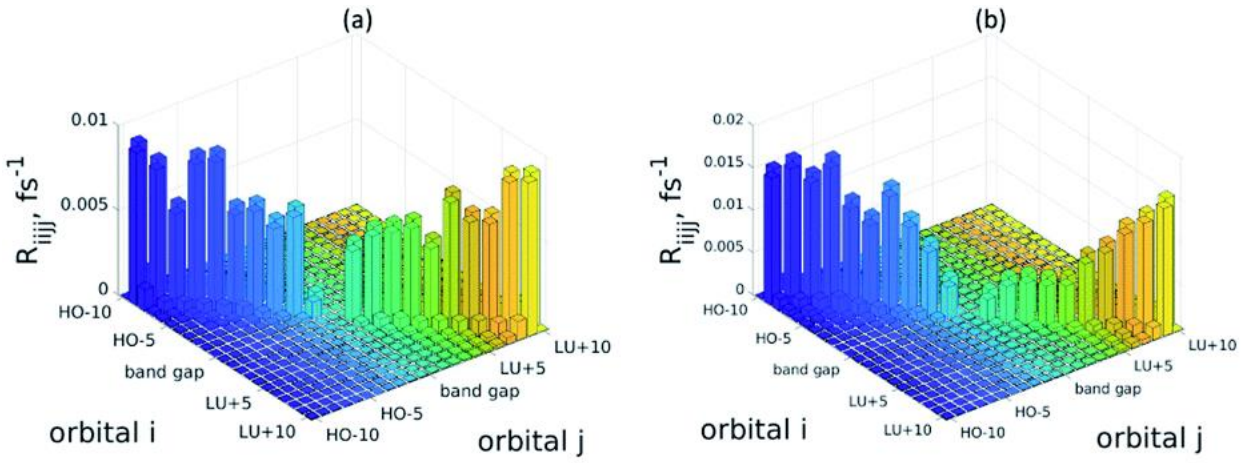

emission
excitation energy, eV
log10(time,ps)

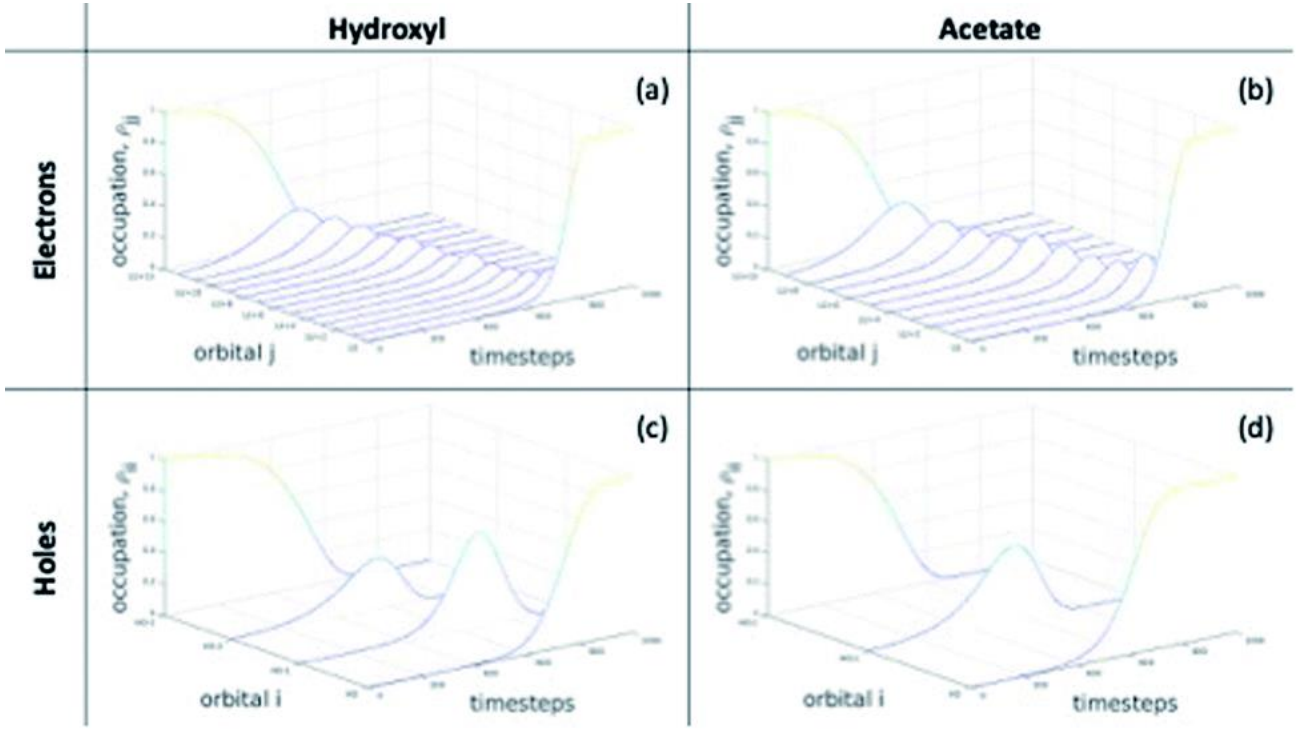

excitation
excitation energy, eV
log10(time,ps)


excitation
excitation energy, eV
log10(time,ps)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-3
-2
-1
0
1
2


200
100
0
-100
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000


Excitation energy (eV)
intensity
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
0
0.05
0.1
0.15
0.2
0.25
0.3


(a)
(b)
R_{iijj}, fs^{-1}
0.01
0.005
0
0.02
0.015
HO-10
HO-5
band gap
LU+5
LU+10
orbital i
orbital j


Hydroxyl
Acetate
Electrons
Holes
(a)
(b)
(c)
(d)
occupation, ρ_{jj}
occupation, ρ_{ii}
orbital j
orbital i
timesteps

Converting Populations of Each Orbital Into a Distribution Over Time & Spatial Position

Computational Chemistry Skills 6/21/2022

Hadassah B. Griffin

Overview

- Redfield Tensor Calculations Completed
- Calculating Electron Dissipative Dynamics from Redfield Equations of Motion
- Matlab script used for code and images that follow: Red_FIELD_MEq_11d_emi6_1f
  - Model included: example from group email
- Skill: visualize how populations of each orbital change over time/in space
- Applications include: charge transfer

Key Variables of Interest

- PPe: list of the populations of electron states (i.e., the orbitals) *i* at time *t*; depends on HOMO and max occupation level (Omax)
- Be: spatial distribution of electrons, and the occupation of electron orbitals over time; built from “bandout” file data and HOMO, Omin, Omax variable information
- **WPe: *(PPe X Be):*** a product of variables PPe and Be, which will help us analyze how population of orbitals changes over time and in space

```
WPe=(((PPe(:,:)'*Be)'));
```

Key Variables of Interest

- PPe:

function of z reads, with $\mathbf{r} = (x,y,z)$

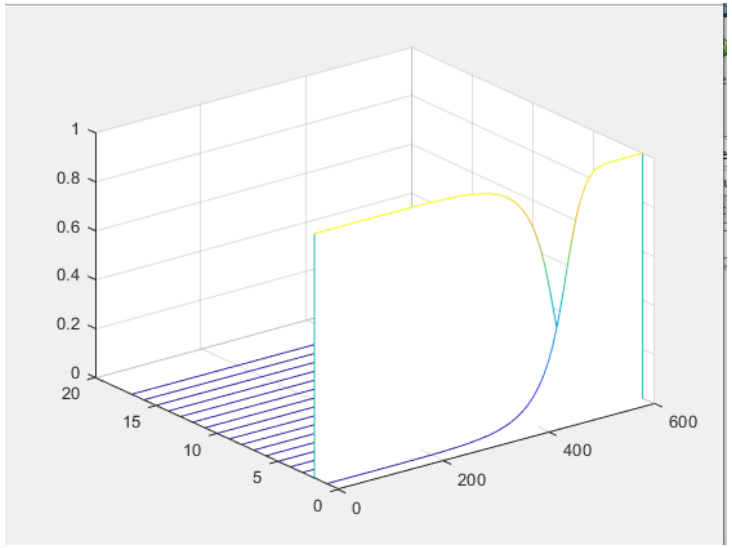
$$P_{\mathrm{CB}}^{(\mathrm{a},\mathrm{b})}(z,t) = \sum_{i,j \geq \mathrm{LU}} \rho_{ij}^{(\mathrm{a},\mathrm{b})}(t) \int \mathrm{d}x\mathrm{d}y\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$$

- Be:
- **WPe: *(PPe X Be):*** a product of matrices PPe and Be, which will help us analyze how population of orbitals changes over time and in space

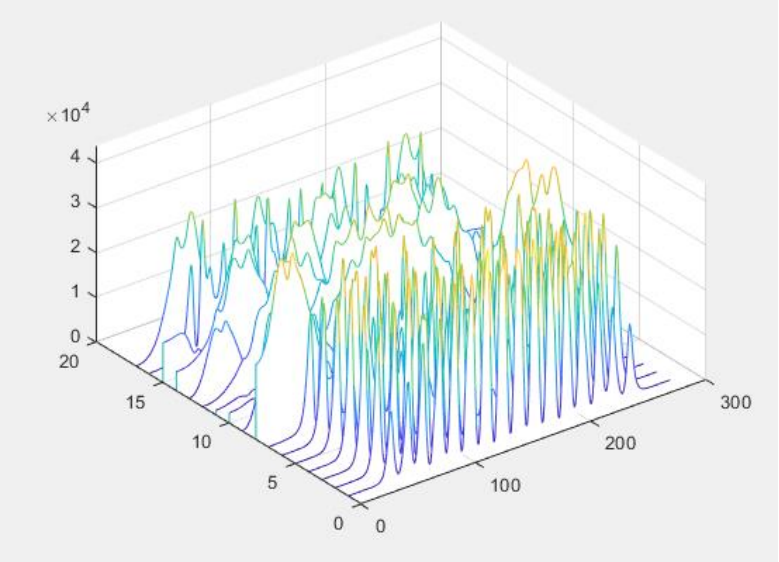
```
WPe=(((PPe(:,:)'*Be)'));
```

Visualization of PPe, Be, Wpe (skewed view, top-down view; all waterfall plots)

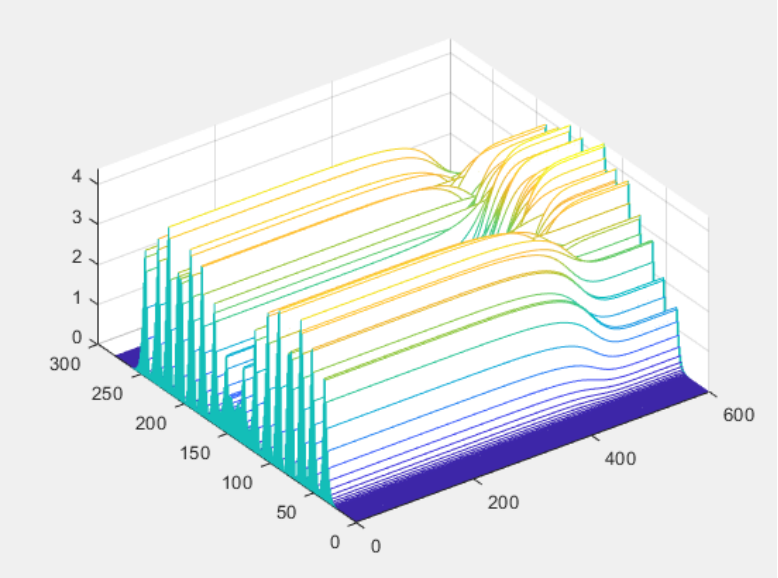
1



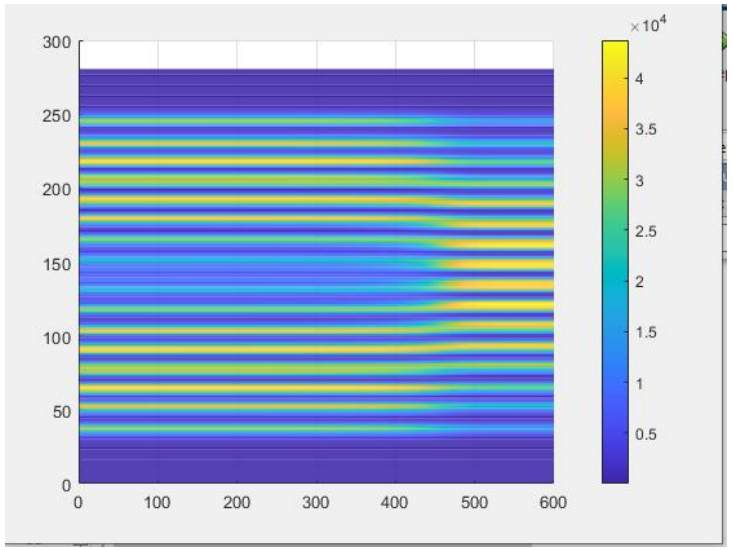
2



3



4



WPe In Code---Steps to Final Visualization

Normalization

```
transfer=(sum(WPe(1:36,:)));
norm=sum(WPe);
plot(transfer)
plot(norm)
plot(transfer.*norm);
plot(transfer.*norm.^(-1));
CT=[time' (transfer.*norm.^(-1))'];
save CT CT -ASCII

zSTEPS=1200;
```

Extract Electron Data as WWPe

```
Zgrid=1:zSTEPS;
Zzgrid=min(Zz)+(max(Zz)-min(Zz))*Zgrid/zSTEPS;
slice1=zeros(size(Zgrid));
WWPe=slice1';
ZWidth=Zz(2)-Zz(1);
for i=1:timeSTEPS;
```

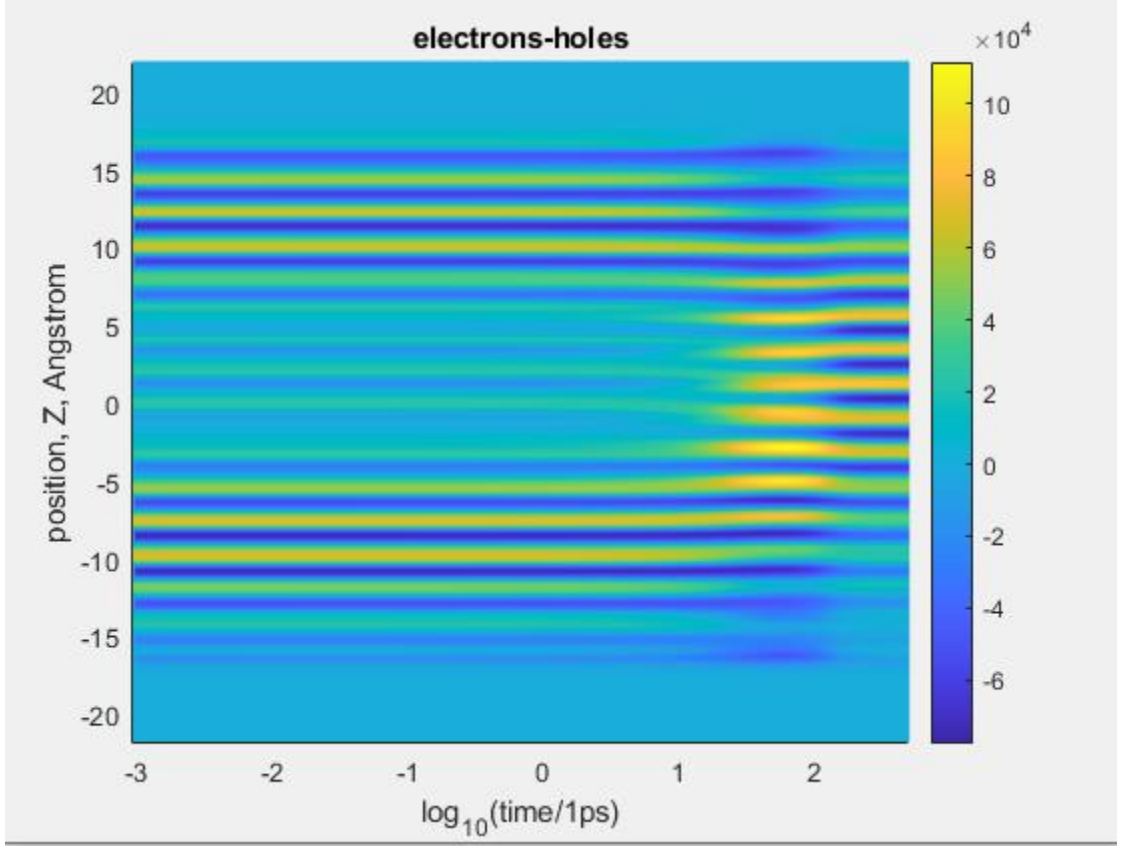
Extract Hole Data as WWPh

```
%---wavepacket in space for holes
slice1=zeros(size(Zgrid));
WWPh=slice1';
ZWidth=Zz(2)-Zz(1);
for i=1:timeSTEPS;
```

Plot Data

```
mesh(log10(time1),Zzgrid,WWPe);axis([-3.05 2.7 -Zzgrid(end) Zzgrid(end)]);view(2)
title('electrons')
xlabel('log_1_0(time/1ps)');
ylabel('position, Z, Angstrom');
figure;
mesh(log10(time1),Zzgrid,WWPh);axis([-3.05 2.7 -Zzgrid(end) Zzgrid(end)]);view(2)
title('holes')
xlabel('log_1_0(time/1ps)');
ylabel('position, Z, Angstrom');
figure
mesh(log10(time1),Zzgrid,WWPe-WWPh);axis([-3.05 2.7 -Zzgrid(end) Zzgrid(end)]);view(2)
xlabel('log_1_0(time/1ps)');
ylabel('position, Z, Angstrom');
title('electrons-holes')
```

Final Visualization and Interpretation



- Brighter values: electron locations
- Darker values: hole locations
- Neutral/0 values: charge density matches same value as ground state before and after excitation
- Charge transfer evidence from seeing if electron/hole locations change over time

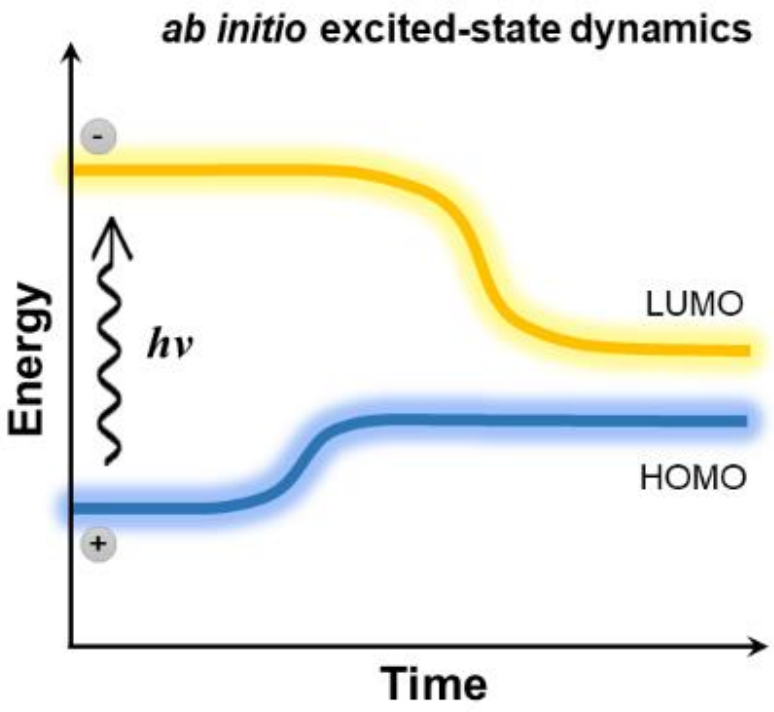
Nonadiabatic couplings without spin

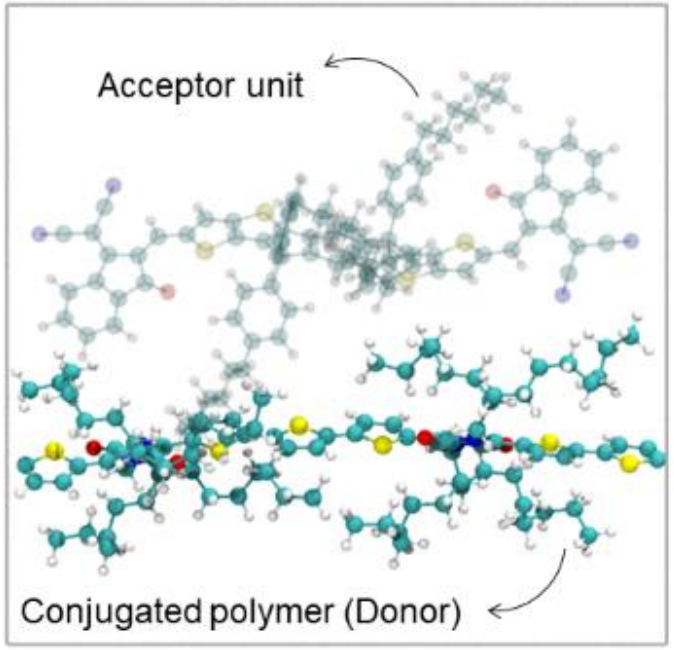
(Relaxation dynamics and distribution of charge as a function of energy and time)

Summer 2022

Nonadiabatic couplings without spin

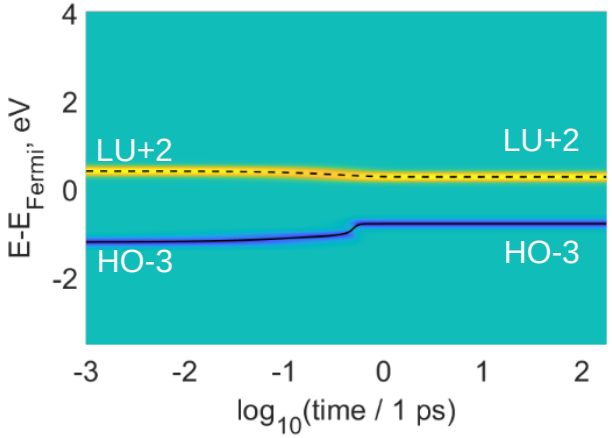
- **Purpose of this methodology?**

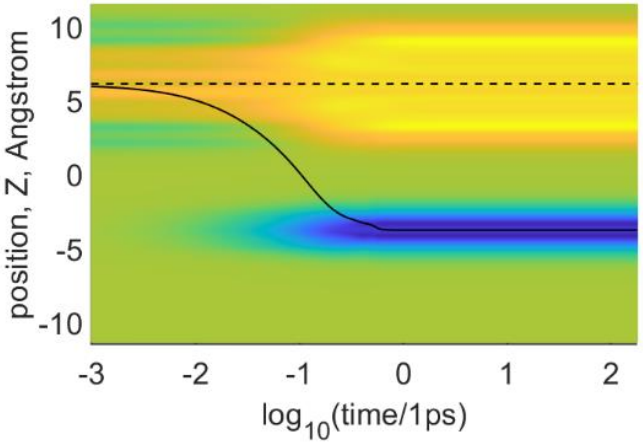


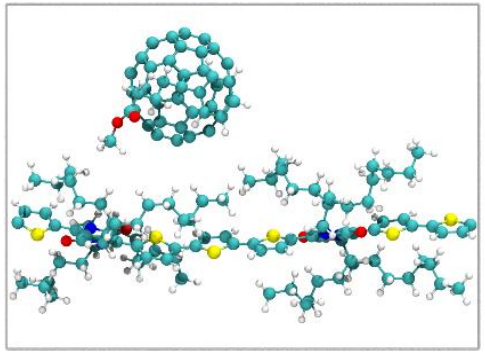


Nonadiabatic couplings without spin

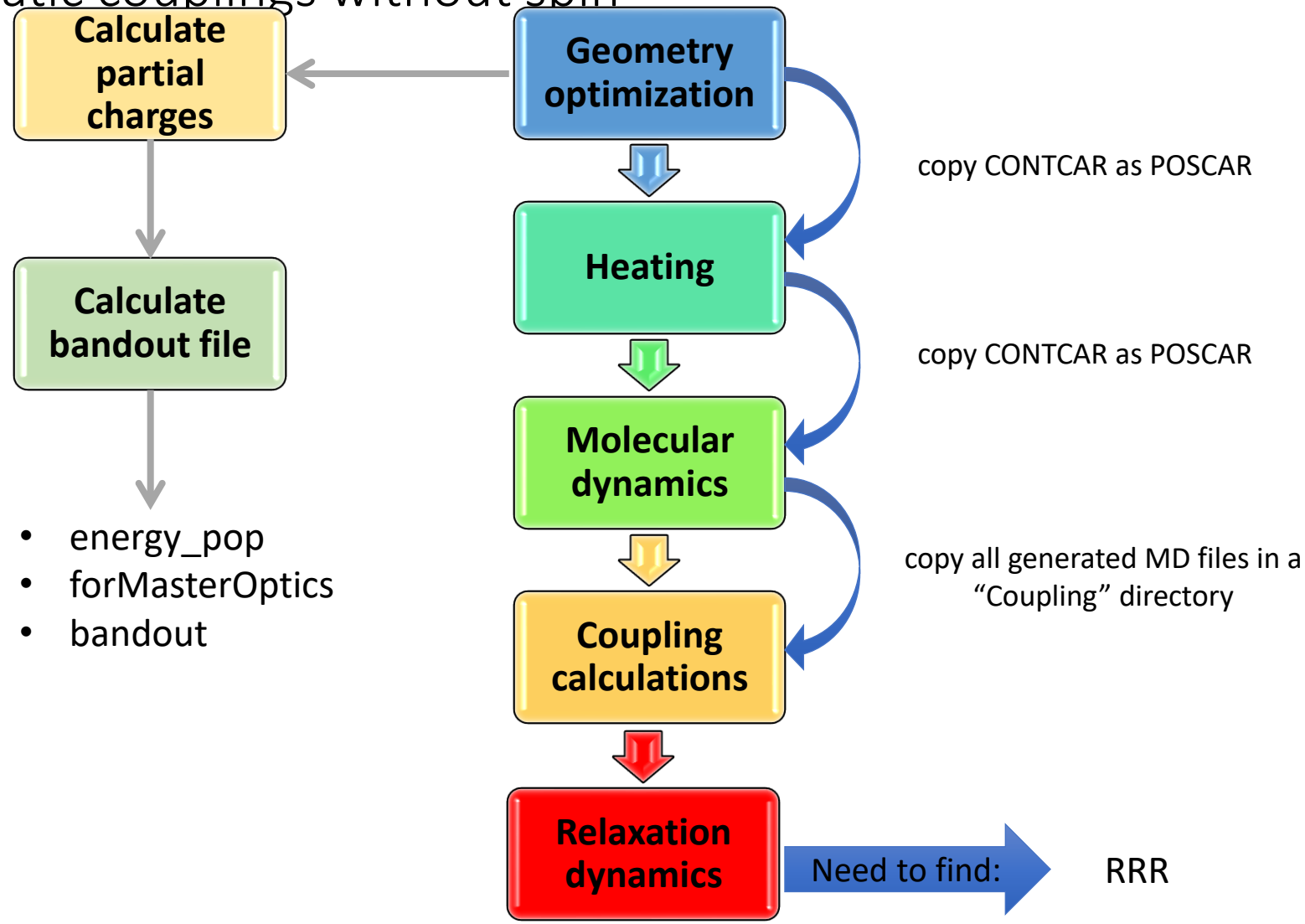
- **Purpose of this methodology?**







Nonadiabatic couplings without spin

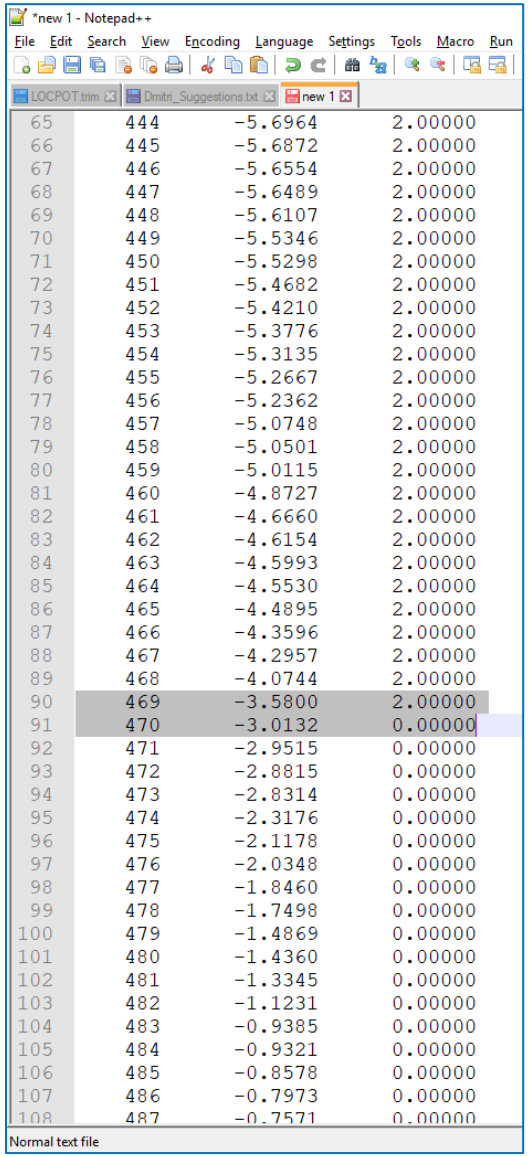


Nonadiabatic couplings without spin

- **What do we need to start the visualization:**

- ❑ **RRR file, was calculated before from the coupling files:**
- ❑ **The “energy_pop” file.**

- ❑ The range of orbitals the you specified in the “energy_pop” file should be consistent through all of your calculations such as bandout and Red field tensor calculations

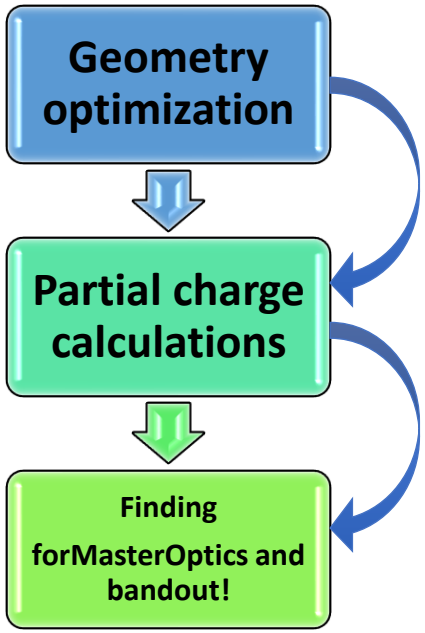


65	444	-5.6964	2.00000
66	445	-5.6872	2.00000
67	446	-5.6554	2.00000
68	447	-5.6489	2.00000
69	448	-5.6107	2.00000
70	449	-5.5346	2.00000
71	450	-5.5298	2.00000
72	451	-5.4682	2.00000
73	452	-5.4210	2.00000
74	453	-5.3776	2.00000
75	454	-5.3135	2.00000
76	455	-5.2667	2.00000
77	456	-5.2362	2.00000
78	457	-5.0748	2.00000
79	458	-5.0501	2.00000
80	459	-5.0115	2.00000
81	460	-4.8727	2.00000
82	461	-4.6660	2.00000
83	462	-4.6154	2.00000
84	463	-4.5993	2.00000
85	464	-4.5530	2.00000
86	465	-4.4895	2.00000
87	466	-4.3596	2.00000
88	467	-4.2957	2.00000
89	468	-4.0744	2.00000
90	469	-3.5800	2.00000
91	470	-3.0132	0.00000
92	471	-2.9515	0.00000
93	472	-2.8815	0.00000
94	473	-2.8314	0.00000
95	474	-2.3176	0.00000
96	475	-2.1178	0.00000
97	476	-2.0348	0.00000
98	477	-1.8460	0.00000
99	478	-1.7498	0.00000
100	479	-1.4869	0.00000
101	480	-1.4360	0.00000
102	481	-1.3345	0.00000
103	482	-1.1231	0.00000
104	483	-0.9385	0.00000
105	484	-0.9321	0.00000
106	485	-0.8578	0.00000
107	486	-0.7973	0.00000
108	487	-0.7571	0.00000

Nonadiabatic couplings without spin

- **What do we need to start calculations:**

- ❑ **forMasterOptics and bandout?**
- ❑ **First we need to do partial charge calculations**



copy CONTCAR as POSCAR
cp ~/bin/INCAR/INCAR-pc ./INCAR

Finding
forMasterOptics and bandout

Nonadiabatic couplings without spin

- **What do we need to start the visualization:**

❑ **INCAR file settings:**

```
LPARD=TRUE       # evaluates partial decomposed charge densities

# Other Parameters

LSEPB=TRUE       # charge density is calculated for every band separately
NBANDS=256       #number of bands in calculation

# Electronic relaxation


ISMEAR=0         #partial occupencies of wavefunction have Gaussian smearing
PREC=Low         #low;med;high
LREAL=.FALSE.    #projection done in reciprocal space
ISYM = 0         #symmetry not considered in calculation
EDIFF=0.0001    #minimum energy difference between electronic iterations

# Ionic Relaxation

IBRION=2         #conjugate-gradient algorithm used to relax ions (bad
NSW=0            #number of ionic steps
POTIM= .5        #time step in fs
EDIFFG=-0.001 #minimum energy difference between ionic iterations

EINT= -5.9 -0.6      →   A range to cover energy_pop
LVTOT    =   .TRUE.
```

Nonadiabatic couplings without spin

- **What do we need to start calculations:**

❑ **forMasterOptics and bandout?**

- cp ~/bin/band_integrate_vasp5.pl .
- vi band_integrate_vasp5.pl
- perl band_integrate_vasp5.pl

(at the end of this step, partial charge files PARCHG.xxx.ALLK will be generated for selected orbitals). The bandout file will be generated here.

```
     499       0.0733      0.00000
kilin@cori09:/global/cfs/cdirs/m1251/vasp/CHEM676_2020/Amir/
kilin@cori09:/global/cfs/cdirs/m1251/vasp/CHEM676_2020/Amir/
eval '(exit $?0)' && eval 'exec perl -S $0 ${1+"$@"}' && eva
#;-*- Perl -*-
#######################################
# this script integrates the CHG file along a single axis
#######################################

# Designate output files

        open (OUT2, ">bandout");

        $fila="PARCHG.0";
        $filc=".ALLK";
#       for ($numb=270;$numb<271;$numb++){
        for ($numb=440;$numb<500;$numb++){

# Setting up file names

            $filb=$numb;

          if ($numb <= 9) {$numb1="00" . $numb};
         if ($numb <= 99) {$numb1="0" . $numb};
          if ($numb >= 100) {$numb1=     $numb};
```

A range to cover energy_pop!

- module swap PrgEnv-intel PrgEnv-gnu
- ~/bin/osc_str_CHEM676.exe
- cp forMasterEq forMasterOptics

Nonadiabatic couplings without spin

- **Double check the size of input files.**

```
kilin@cori09:/global/cfs/cdirs/m1251/vasp/CHEM676_2020/Amir/PROJECT_PC/FOLLOWUP/DPP_PCBM/MD/BANDOUTS> wc energy_pop
  60  180 2040 energy_pop
kilin@cori09:/global/cfs/cdirs/m1251/vasp/CHEM676_2020/Amir/PROJECT_PC/FOLLOWUP/DPP_PCBM/MD/BANDOUTS> wc forMasterOptics
   60  3600 93660 forMasterOptics
kilin@cori09:/global/cfs/cdirs/m1251/vasp/CHEM676_2020/Amir/PROJECT_PC/FOLLOWUP/DPP_PCBM/MD/BANDOUTS> wc bandout
    60   8556 144596 bandout
kilin@cori09:/global/cfs/cdirs/m1251/vasp/CHEM676_2020/Amir/PROJECT_PC/FOLLOWUP/DPP_PCBM/MD/BANDOUTS>
```

- Bandout file contains the same information as “PARCHG.xxx.ALLK ”.
- They are results of integration of each 3D PARCHG over X and Y.

Nonadiabatic couplings without spin

- **Execute the Matlab file:**

❑ **In Matlab directory we should have:**

✓ RRR

✓ energy_pop

✓ bandout

✓ forMasterOptics

✓ RATE_Red_FIELD_MEq_11d_emi6_1g_version_Summer_2022.m

Nonadiabatic couplings without spin

- **Run the Matlab codes to calculate relaxation dynamics**

❑ **Matlab script "**Red_FIELD_MEq_11d_emi6_1f.m**" or "**RATE_Red_FIELD_MEq_11d_emi6_1g_version_Summer_2022.m**":**

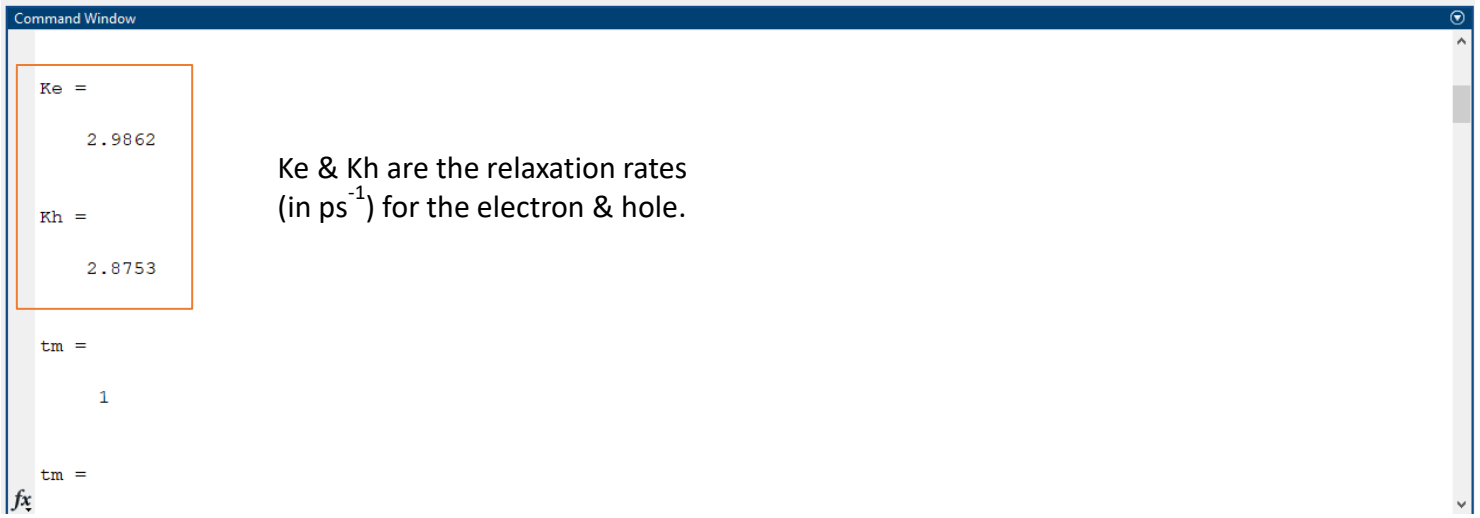
```
clc
clear all
close all

% Eexc=0.3;%3.5;%eV
Width=.1;

timeSTEPS=600

bandoutOrig=load('bandout');
energy_pop=importdata('energy_pop');
bandout=abs(bandoutOrig(:,2:end));
[m_band,n_band]=size(bandout);

Zsteps=n_band;  % number of steps along Z (+1)
Zsize= 23; % cell size along Z from POSCAR

Omin=energy_pop(1,1); % Smallest orbital number in energy_pop
Omax=energy_pop(end,1); % Largest orbital number in energy_pop
n_Orbital=numel(energy_pop(:,1)); % Number of orbitals

%initial electron
% Finde the "HOMO" in energy_pop
for i=1:n_Orbital
    if energy_pop(i,3)<0.5
        HOMO=energy_pop(i-1,1);
       break
    end
end
LUMO=HOMO+1;

% Selected initial transitions for iH and iE
Occupied_Orb=   HOMO-3
Unoccupied_Orb= LUMO+2
```

Select the initial transition based on the highest value of oscillator strength in "OS_STRENGTH" file.

469	473	1.91527228	0.8130	2.0000	0.0000	1.3194	-5.0524	2.1741
466	472	0.97081346	1.7198	2.0000	0.0000	0.0884	-0.0163	0.0066
461	477	0.76628863	2.9368	2.0000	0.0000	0.3738	0.1459	1.8395
461	470	0.68394278	1.8236	2.0000	0.0000	0.0351	-0.1257	0.0351
465	473	0.64480920	1.8338	2.0000	0.0000	0.2551	-2.1116	0.4652
463	470	0.53752501	1.6081	2.0000	0.0000	-0.0261	0.0053	-0.0044
464	475	0.38692201	2.6863	2.0000	0.0000	0.3729	-0.9177	0.9892
462	477	0.36538379	2.7533	2.0000	0.0000	0.6288	-1.0864	0.4786
464	486	0.31370063	3.7817	2.0000	0.0000	0.3333	0.3495	0.9460
462	483	0.30301199	3.6694	2.0000	0.0000	0.2600	-0.2312	0.9992
467	473	0.24945212	1.6429	2.0000	0.0000	0.0224	0.0971	0.0670
461	472	0.24211756	2.0779	2.0000	0.0000	0.0287	0.7621	-0.9976
467	476	0.23115498	2.4617	2.0000	0.0000	0.1142	-1.0746	0.2959
462	470	0.21720914	1.6401	2.0000	0.0000	-0.0030	0.0136	-0.0201
462	471	0.19433876	1.6730	2.0000	0.0000	-0.0415	0.0622	0.1201
463	478	0.18837127	2.9420	2.0000	0.0000	-0.0708	-0.3985	-0.8285
456	474	0.18720686	3.0022	2.0000	0.0000	-0.0876	0.8248	-0.2690
450	470	0.18093864	2.4745	2.0000	0.0000	-0.0456	-0.5001	-0.8259
466	482	0.17789103	3.4518	2.0000	0.0000	-0.0882	-0.0493	0.0180
461	487	0.17546004	4.0256	2.0000	0.0000	-0.1806	0.2082	-0.7175
451	488	0.17072121	4.8583	2.0000	0.0000	0.1753	-0.1211	0.6494
461	478	0.16601288	3.1575	2.0000	0.0000	0.0529	0.6472	-0.5396
463	483	0.15776397	3.6374	2.0000	0.0000	-0.2317	-0.2672	-0.5788
466	477	0.15405094	2.5787	2.0000	0.0000	0.8205	0.0202	-0.0902
466	471	0.15251968	1.4984	2.0000	0.0000	-0.1396	0.0411	-0.0340
465	471	0.15241437	1.5988	2.0000	0.0000	-0.1791	-0.1695	0.4012
461	479	0.15013712	3.3800	2.0000	0.0000	0.5738	0.2622	-0.0005
466	485	0.14982642	3.6184	2.0000	0.0000	0.0925	-0.3608	0.6502
463	477	0.14068938	2.7213	2.0000	0.0000	-0.5817	0.3108	-0.5179
450	488	0.13521664	4.8728	2.0000	0.0000	-0.1755	0.0805	-0.5588
454	474	0.12934594	3.0241	2.0000	0.0000	-0.0065	-0.7356	0.1480
468	476	0.12540796	2.0155	2.0000	0.0000	0.0809	-0.0604	-0.0400

Nonadiabatic couplings without spin

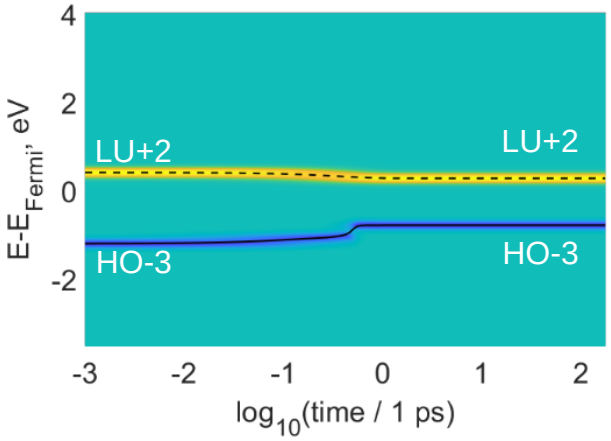
- **After finished the simulations, you should be able to see rate of electron and hole relaxation in the command window:**

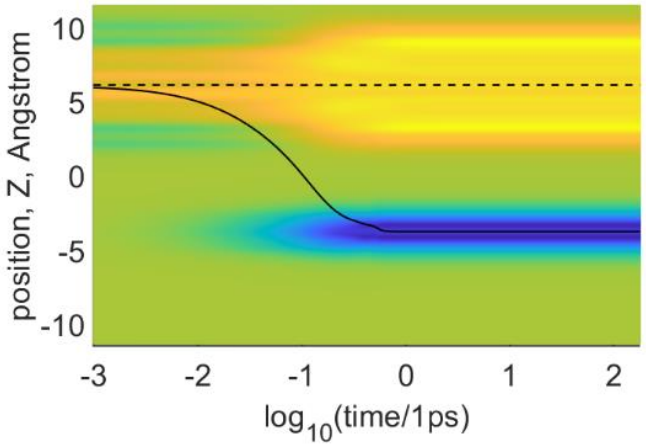


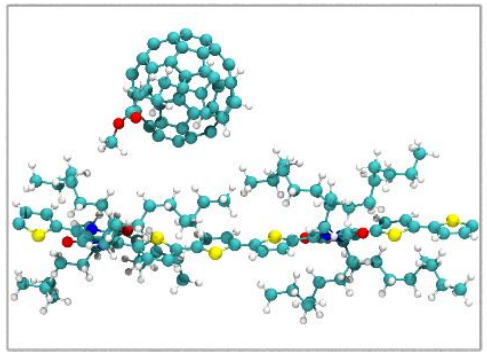
Ke & Kh are the relaxation rates (in ps^{-1}) for the electron & hole.

Nonadiabatic couplings without spin

- **Code will produce the Relaxation dynamics and distribution of charge as a function of energy and time:**

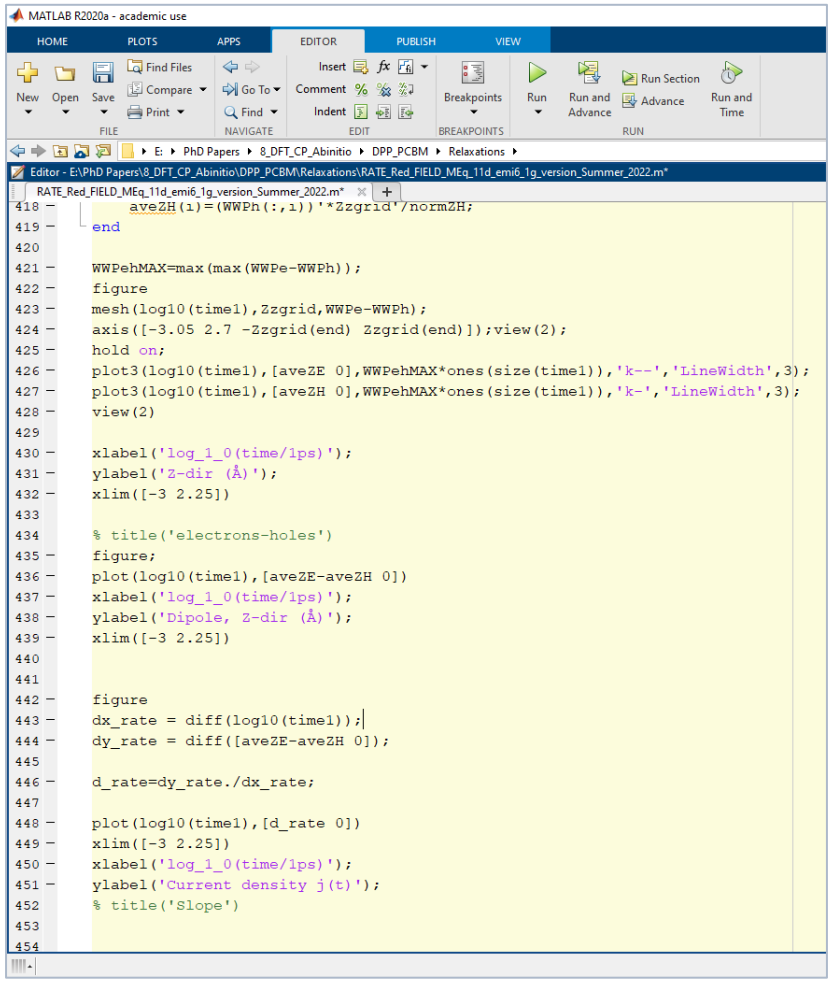




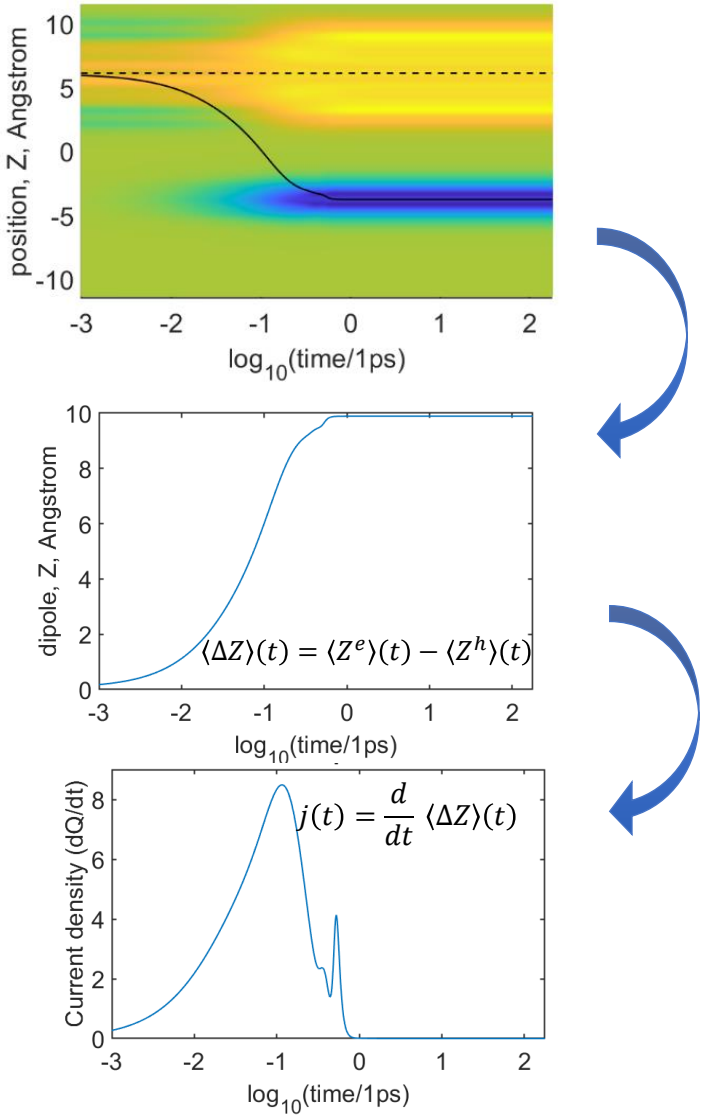


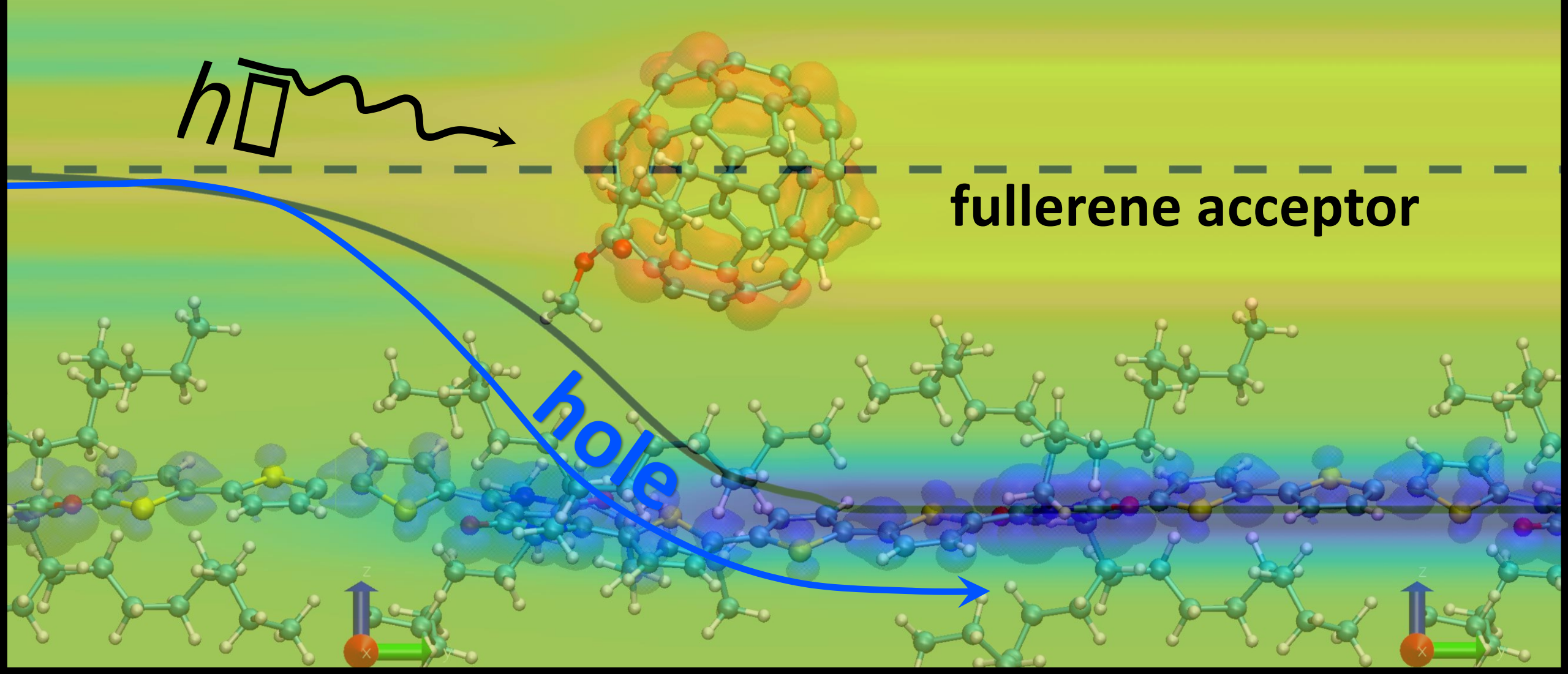
Nonadiabatic couplings without spin

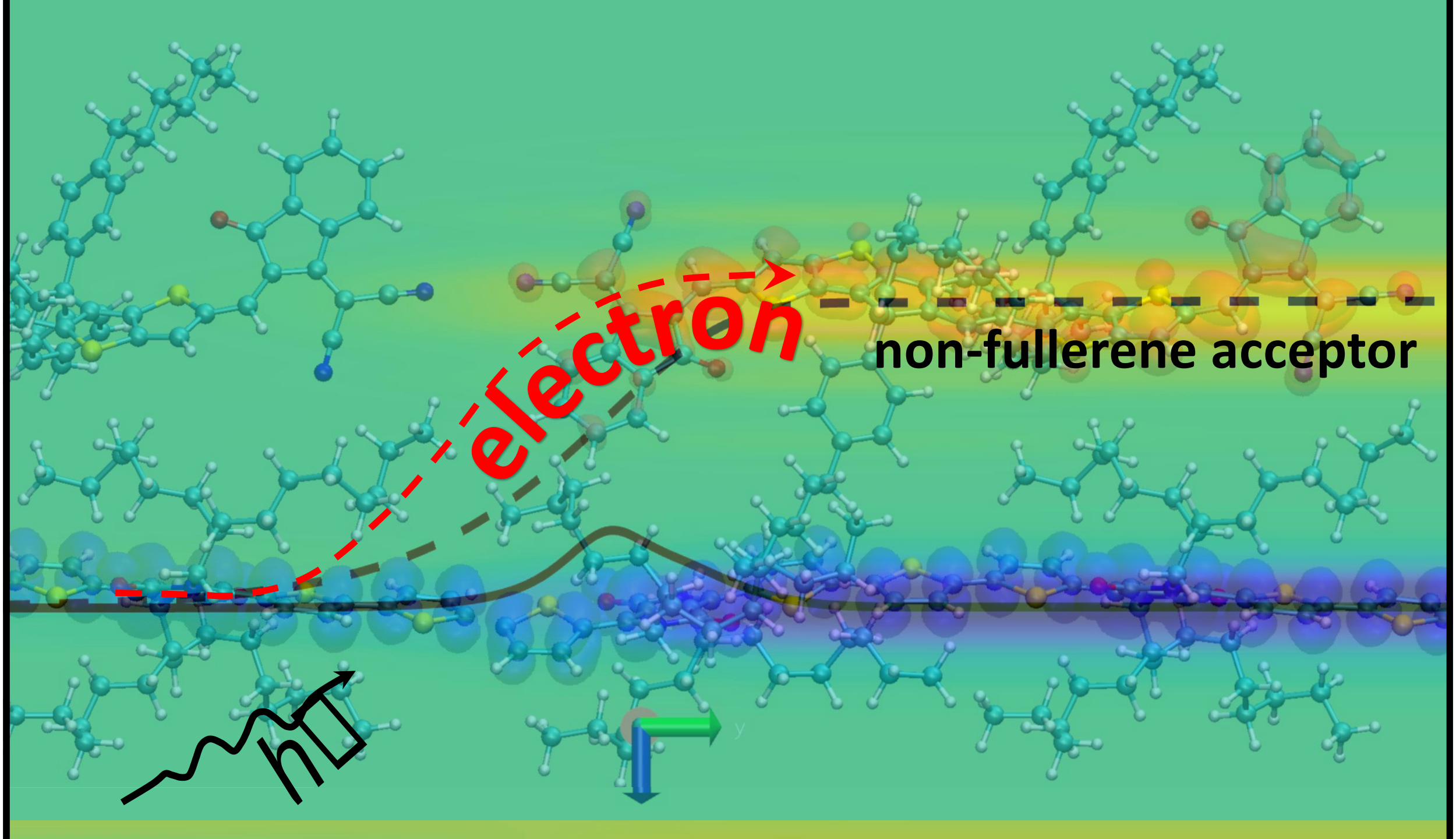
- **Quantify charge transfer at the interface:**

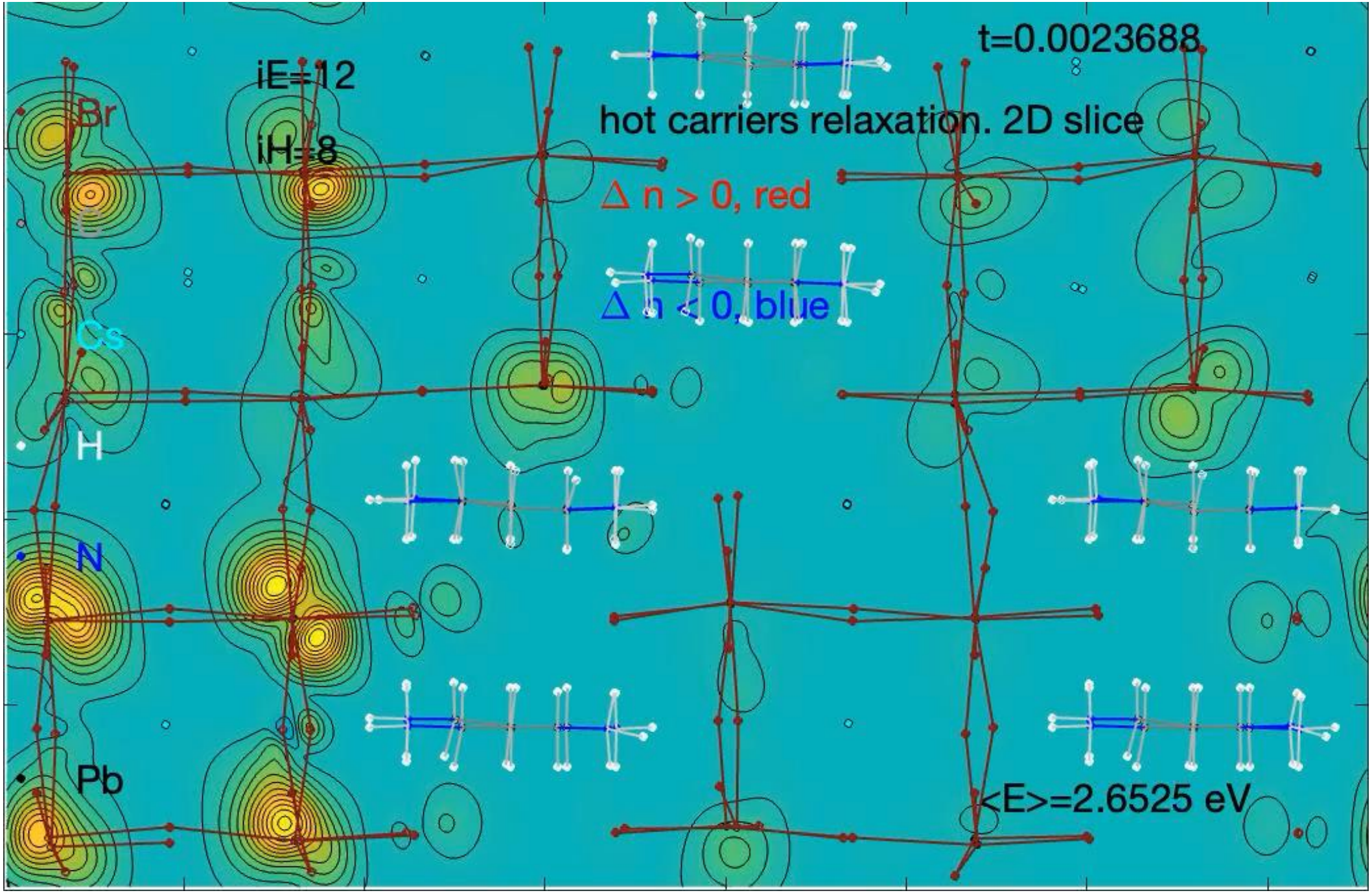



```
        aveZH(i)=(WWPh(:,i))'*Zzgrid'/normZH;
    end

    WWPehMAX=max(max(WWPe-WWPh));
    figure
    mesh(log10(time1),Zzgrid,WWPe-WWPh);
    axis([-3.05 2.7 -Zzgrid(end) Zzgrid(end)]);view(2);
    hold on;
    plot3(log10(time1),[aveZE 0],WWPehMAX*ones(size(time1)),'k--','LineWidth',3);
    plot3(log10(time1),[aveZH 0],WWPehMAX*ones(size(time1)),'k-','LineWidth',3);
    view(2)

    xlabel('log_1_0(time/1ps)');
    ylabel('Z-dir (Å)');
    xlim([-3 2.25])

    % title('electrons-holes')
    figure;
    plot(log10(time1),[aveZE-aveZH 0])
    xlabel('log_1_0(time/1ps)');
    ylabel('Dipole, Z-dir (Å)');
    xlim([-3 2.25])


    figure
    dx_rate = diff(log10(time1));
    dy_rate = diff([aveZE-aveZH 0]);

    d_rate=dy_rate./dx_rate;

    plot(log10(time1),[d_rate 0])
    xlim([-3 2.25])
    xlabel('log_1_0(time/1ps)');
    ylabel('Current density j(t)');
    % title('Slope')
```




hν
fullerene acceptor
hole


electron
non-fullerene acceptor
hν

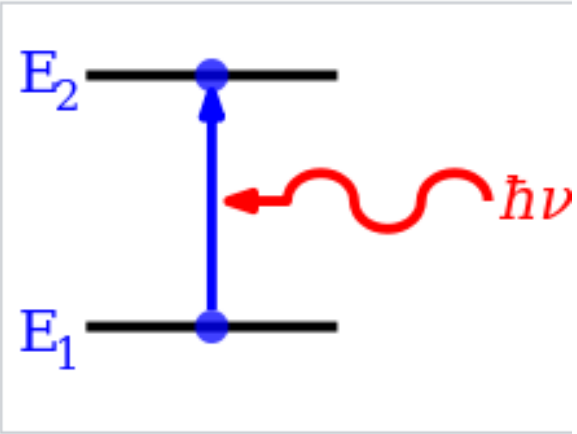

t=0.0023688
iE=12
iH=8
hot carriers relaxation. 2D slice
Δ n > 0, red
Δ n < 0, blue
Br
Cs
H
N
Pb
<E>=2.6525 eV

Photoluminescence

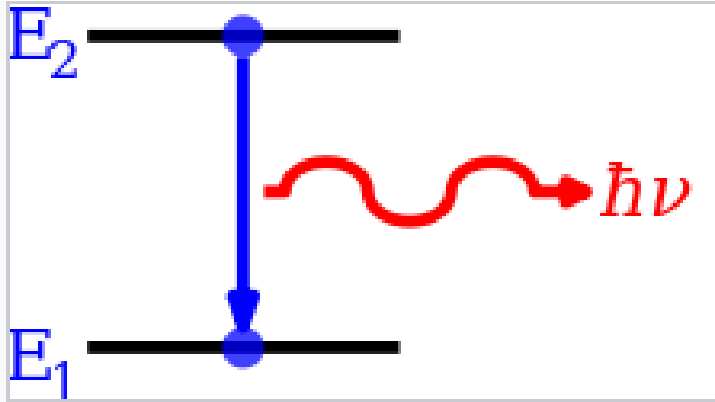
William Tupa

Absorption vs Emission

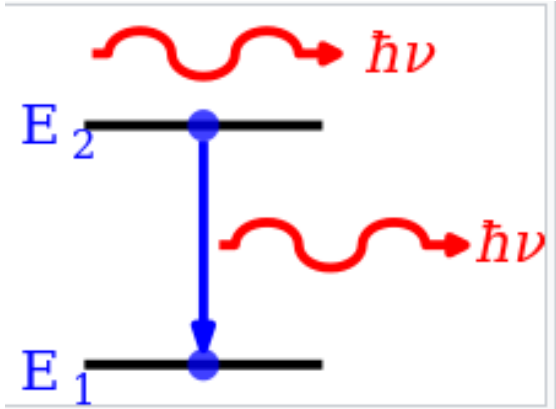
- Absorption: Matter takes in a photon to then move an electron to a higher energy level.
- Spontaneous Emission: Matter releases a photon to drop a photon to a lower energy level.
- Stimulated Emission: Same as spontaneous emission but now this happens when the matter when a photon goes by it. The two photons have the same direction, frequency and polarization.



Schematic diagram of atomic absorption



Schematic diagram of atomic spontaneous emission



Schematic diagram of atomic stimulated emission

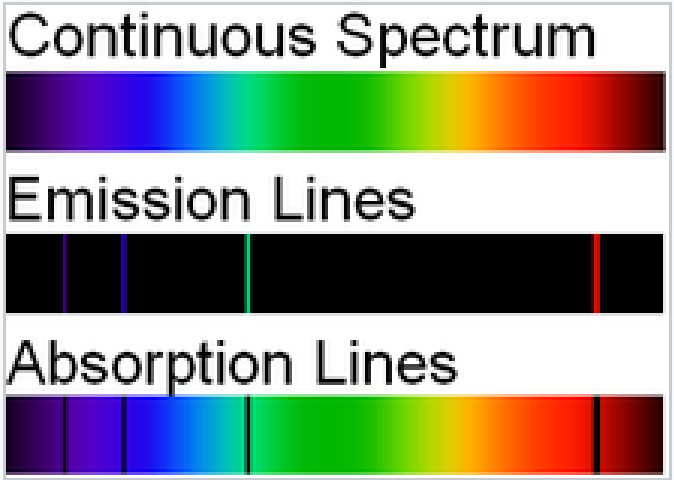
Einstein Coefficients

- Measure how likely a photon is will be absorbed or emitted from an atom.
- A_{xy} would be the spontaneous emission probability of a transition from level x to level y.
- B_{xy} would be the absorption or spontaneous emission probability of a transition from level x to level y.
- g_x is the degeneracy of level x.
- f_{xy} is the oscillator strength.

$$B_{12} = \frac{e^2}{4\epsilon_0 m_e h\nu} f_{12}$$

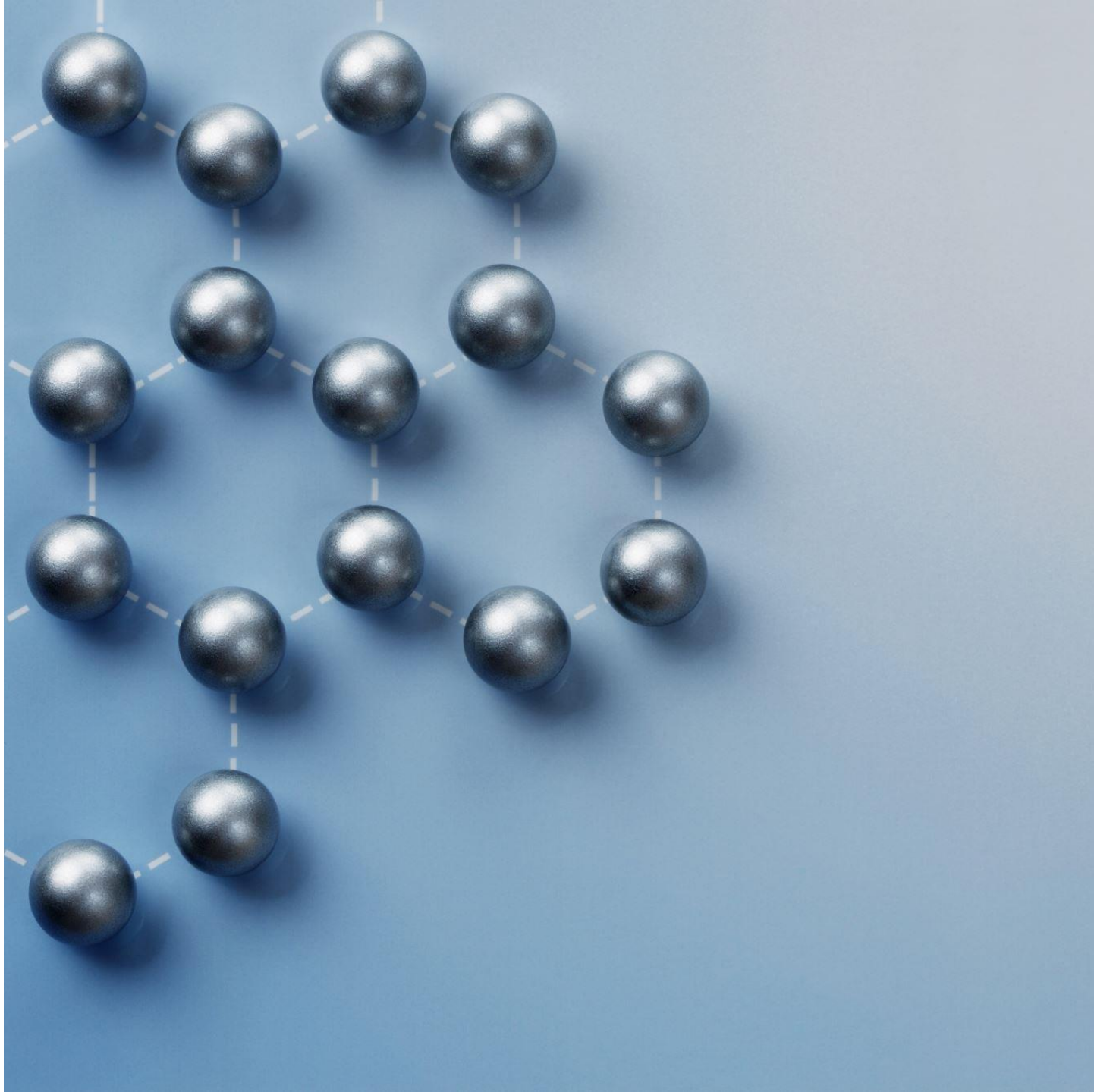
$$B_{21} = \frac{e^2}{4\epsilon_0 m_e h\nu} \frac{g_1}{g_2} f_{12}$$

$$A_{21} = \frac{2\pi\nu^2 e^2}{\epsilon_0 m_e c^3} \frac{g_1}{g_2} f_{12}$$



Emission lines and absorption lines compared to a continuous spectrum

Why the PL module of the Redfield code has a cycle over timesteps?



Electronic Dynamic

- changing initial conditions of electron dynamics by tags iE and iH
- how to find rates of electron and hole relaxation for each iE, iH

Needed Files

Script Name: **Red_FIELD_MEq_11d_emi6_1f.m**
Input Files -
Input_overlap
Energy_pop, forMasteroptic
RRR
Bandout (std) / Bandout2D (ncl)
Outputs –
Excited state relaxation in energy and space domains
Rates of relaxation from HO-x to HO and LU+y to LU

```
timeSTEPS=600;

iH=5;%12;%22;%31;%3;%14;%8;%11;%3;%22;%14;%8;%19;%8
%initial hole
iE=5;%8;%2;%4;%3;%5;%3;%8;%3
%initial electron
HOMO=472
LUMO=HOMO+1
Omin=463
Omax=482
KKKmax=Omax-Omin+1;
```

✓ Set the Initial condition according to oscillator strength

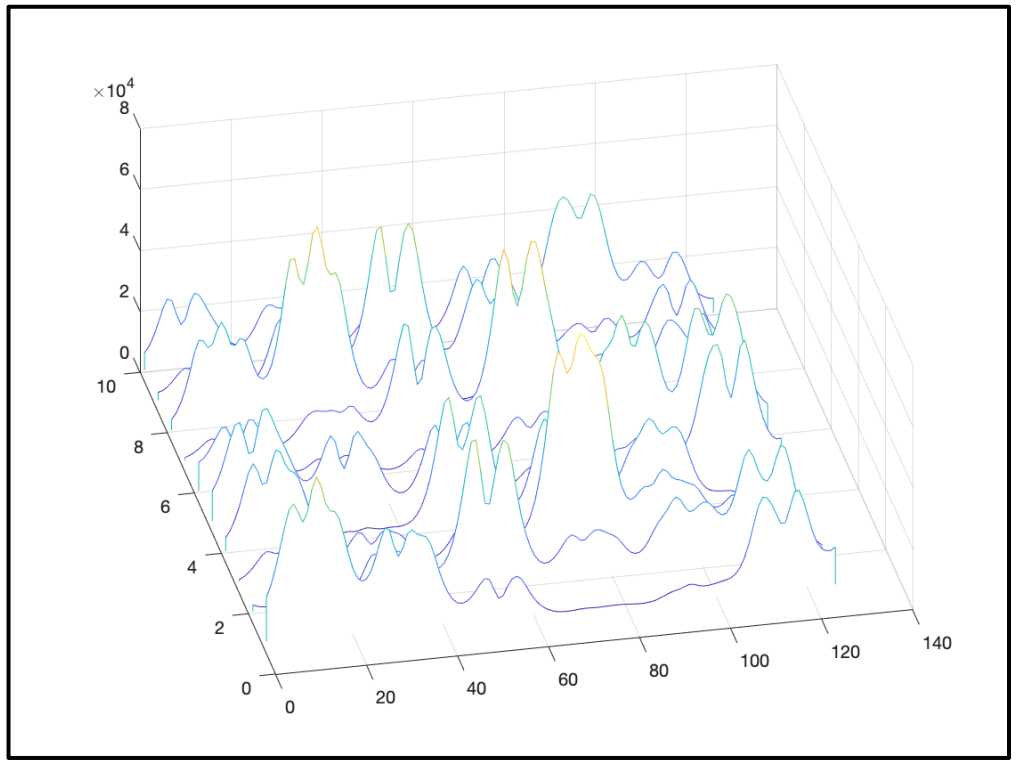
```
% for master Eq
NUM=load('energy_pop')*[1 0 0]';
energy_pop=load('energy_pop')*[0 1 0]';
POP=load('energy_pop')*[0 0 1]';

forME=load('RRR');
forMEoptic1=load('forMasterOptics');

count=1;
for i=1:KKKmax;
    for j=1:KKKmax;
     forMEoptic(i,j)=forMEoptic1(count);
     count=count+1;
 end;
end;
```

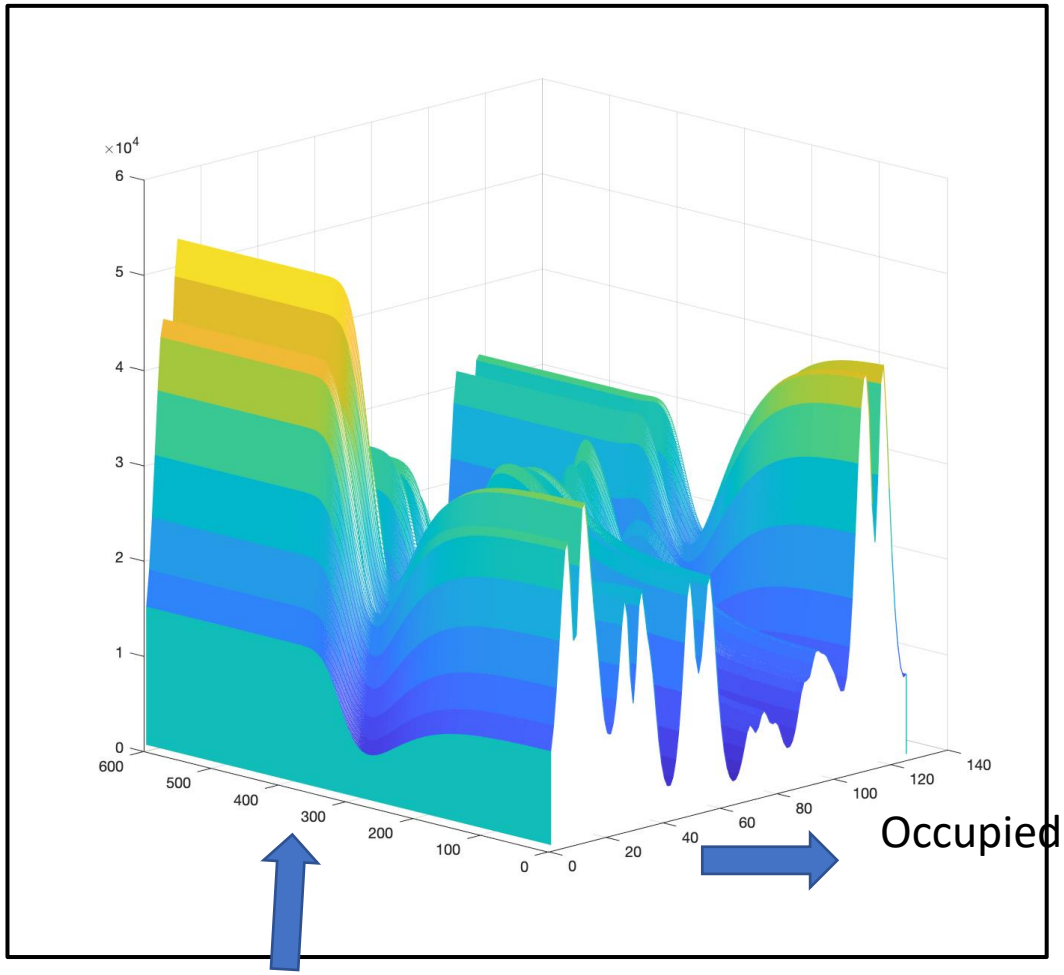
```

Voltage=0;%-10;%Volt
Temperature=1;%K;
Zsteps=126;%400;  % number of steps along Z (+1)
Zsize= 19.5527347856869191; % cell size along Z from POSCAR

Z=1:Zsteps;Zz=Z/Zsteps*Zsize-Zsize/2;
```

size(bandout)= 20 126

28 June
Group Meeting

Results of the Electronic Dynamic Calculation

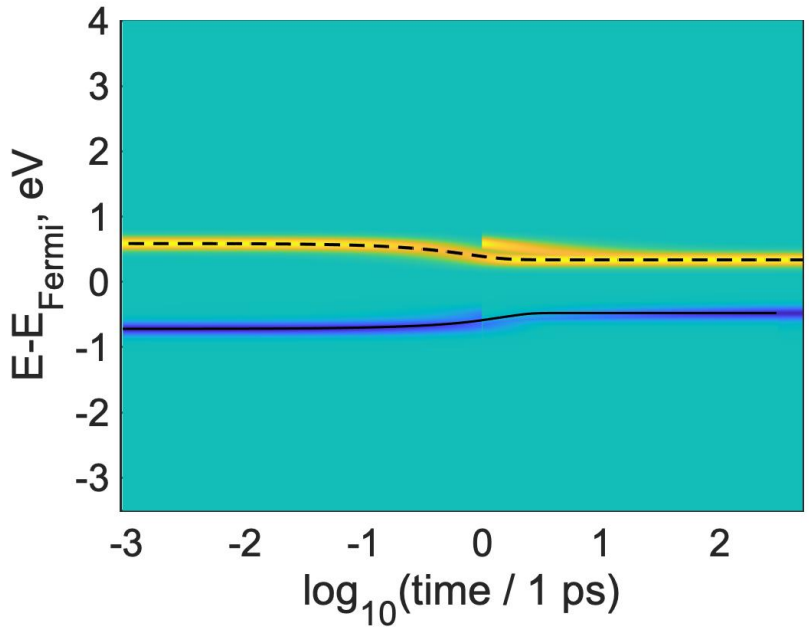


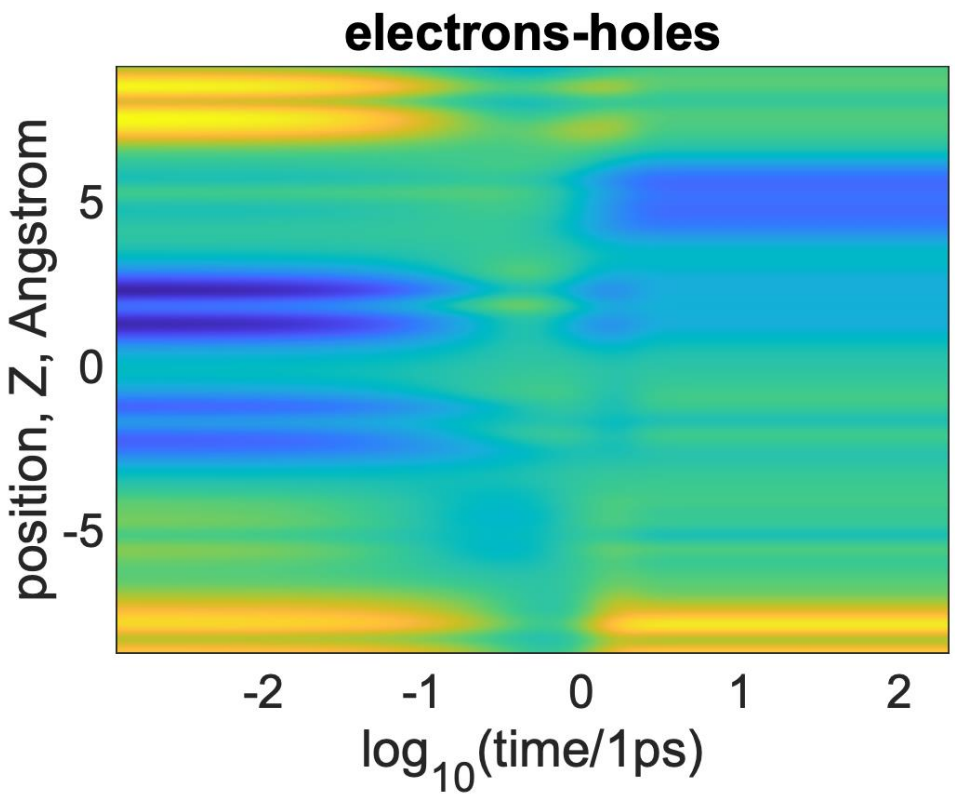


Occupied orbital

Time steps

```
Ke =

    1.5594

Kh =

    0.9572
```





$$E(\hbar\omega, t) = \sum_{j>i} f_{ij}\,\delta(\hbar\omega - \hbar\omega_{ij})\{\rho_{jj}(t) - \rho_{ii}(t)\}$$

```
for Oj=1:Omax-Omin+1; %Oj=source orbital in VASP-notation
for Ok=Oj+1:Omax-Omin; %Ok=target orbital in VASP-notation
    iH=HOMO-Omin-j;
    iE=k+1-HOMO;
    eEX=energy_pop(Ok)-energy_pop(Oj);
        %Ee(iE)-Eh(iH);
        %energy of excitation
    popEX=exPP1(tm,Ok)-exPP1(tm,Oj);

            opEX=exPP(tm,Ok)*exPP(tm,Oj);
            % this is for Prezhdo-exciton, product

        %(PPe(iE,i))-(PPh(iH,i)); % population of excitation
    FosEX=forMEoptic(Oj,Ok) ; % oscillator strength of excitation
    slice2=slice2+popEX*exp(-((eEX-Egrid)/(Width/3)).^2);
```

$$E(\hbar\omega, t) = \sum_{j>i} f_{ij}\,\delta(\hbar\omega - \hbar\omega_{ij})\{\rho_{jj}(t) - \rho_{ii}(t)\}$$

```
            if Ok>(HOMO-Omin+1)
                if Oj<(HOMO-Omin+2)
                    % this is for Prezhdo-exciton, product
                    slice3=slice3+popEX*exp(-((eEX-Egrid)/(Width/3)).^2);
                end;
            end;

            slice=slice+FosEX*popEX*exp(-((eEX-Egrid)/(Width/3)).^2);
            if popEX>0
                slice1=slice1+FosEX*popEX*exp(-((eEX-Egrid)/(Width/3)).^2);
            end;
        end;
        end;
```

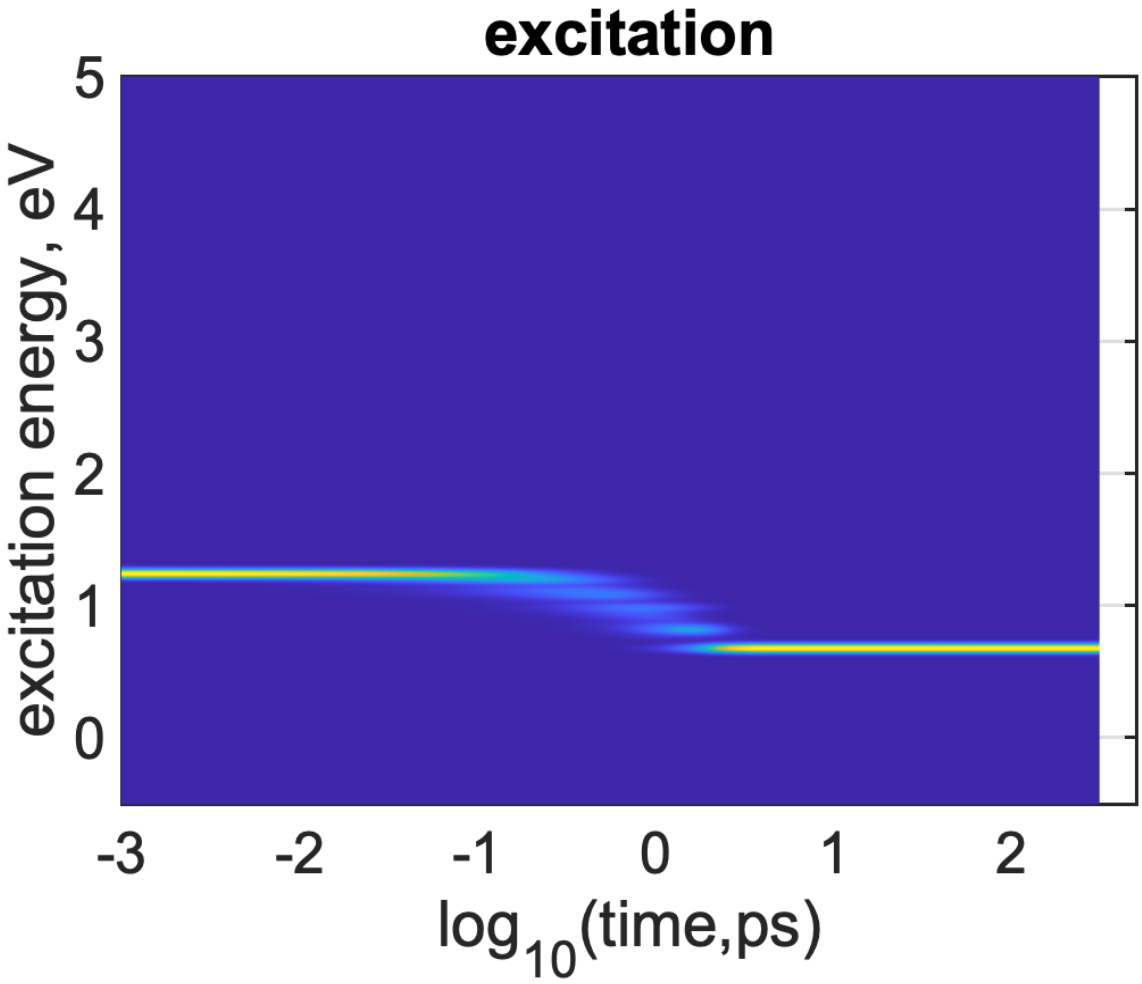
```
514        exciton=[exciton
515                 slice];
516        emission=[emission
517                 slice1];
518              justexciton=[justexciton
519                          slice2];
520              prezhdoexciton=[prezhdoexciton
521                          slice3];
522
523    end;
```

$$E(\hbar\omega) = \frac{1}{T}\int_0^T E(\hbar\omega, t)dt$$

```
%compute integrated emission
dt1=[dt(1) dt];
Iemission=emission'*dt1';
WLgrid=(1241*Egrid.^(-1))';
PL=[Egrid' WLgrid Iemission];
save -ASCII PL PL
```

Results of the Electronic Dynamic Calculation

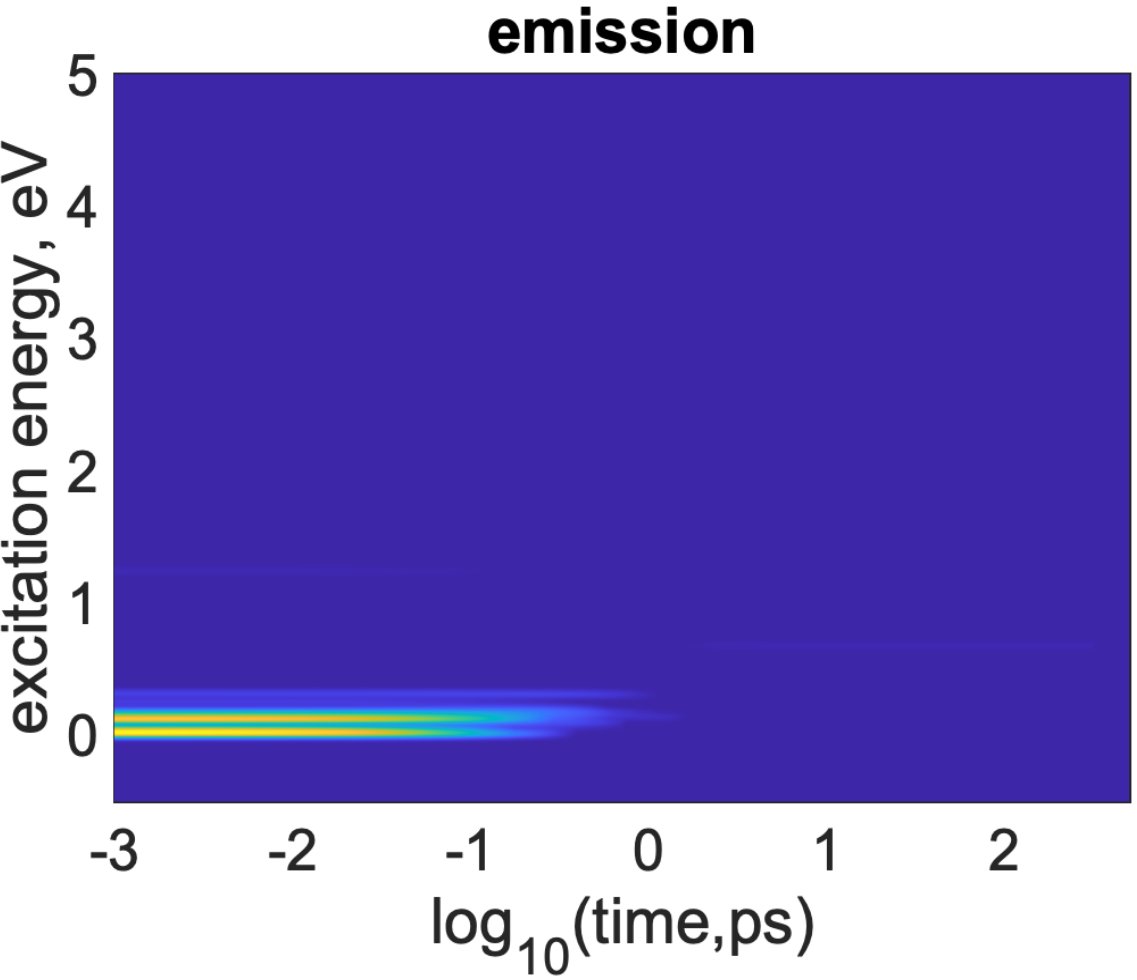
$$P(\varepsilon, t) = \sum_{j \leq HO} \sum_{i \geq LU} \rho_{ii}(t) \cdot \rho_{jj}(t) \delta\left(\varepsilon_i^E - \varepsilon_j^E - \varepsilon\right)$$

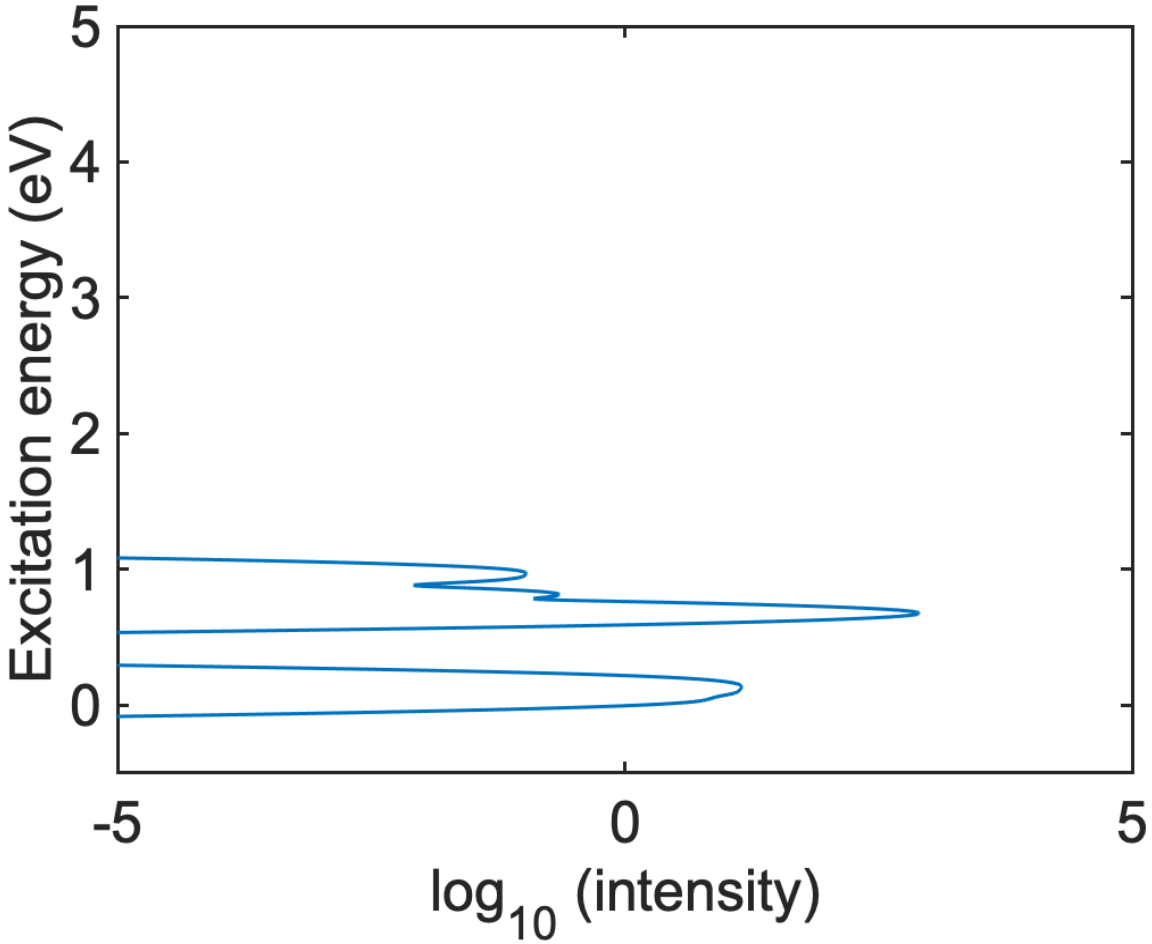


Results of the Electronic Dynamic Calculation

$$E(\hbar\omega, t) = \sum_{j>i} f_{ij}\delta(\hbar\omega - \hbar\omega_{ij})\{\rho_{jj}(t) - \rho_{ii}(t)\}$$

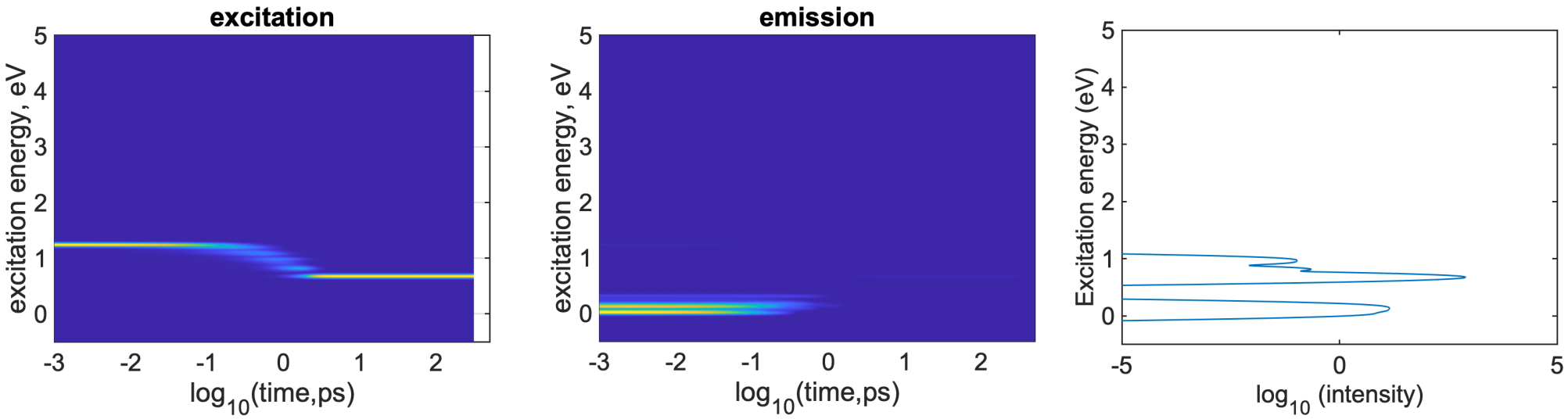
$$E(\hbar\omega) = \frac{1}{T}\int_0^T E(\hbar\omega, t)dt$$

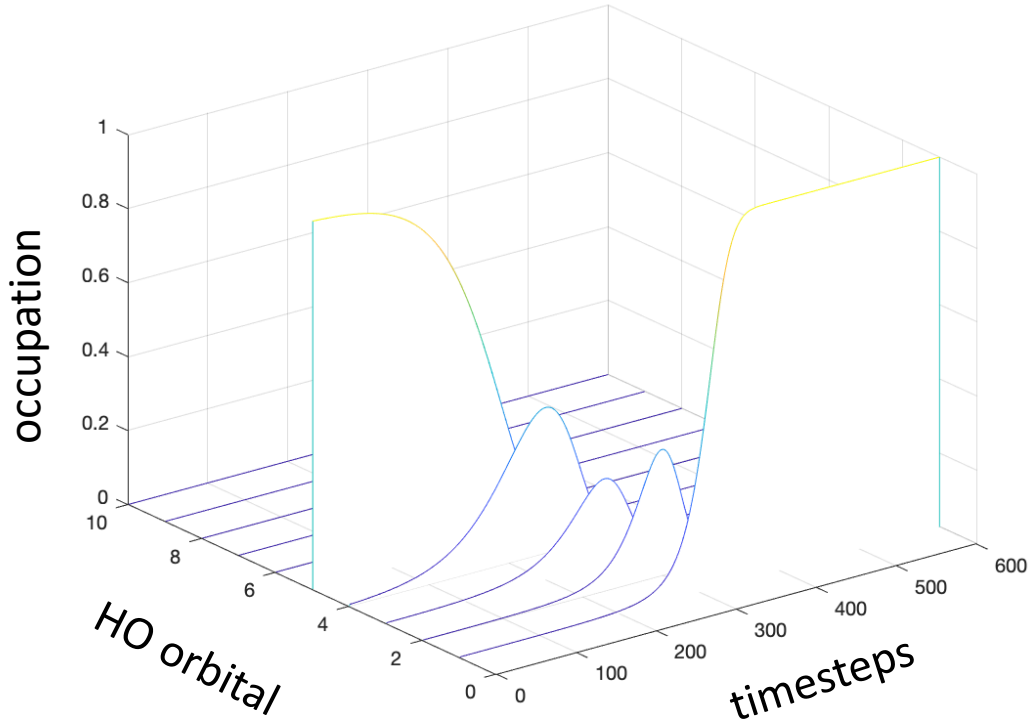




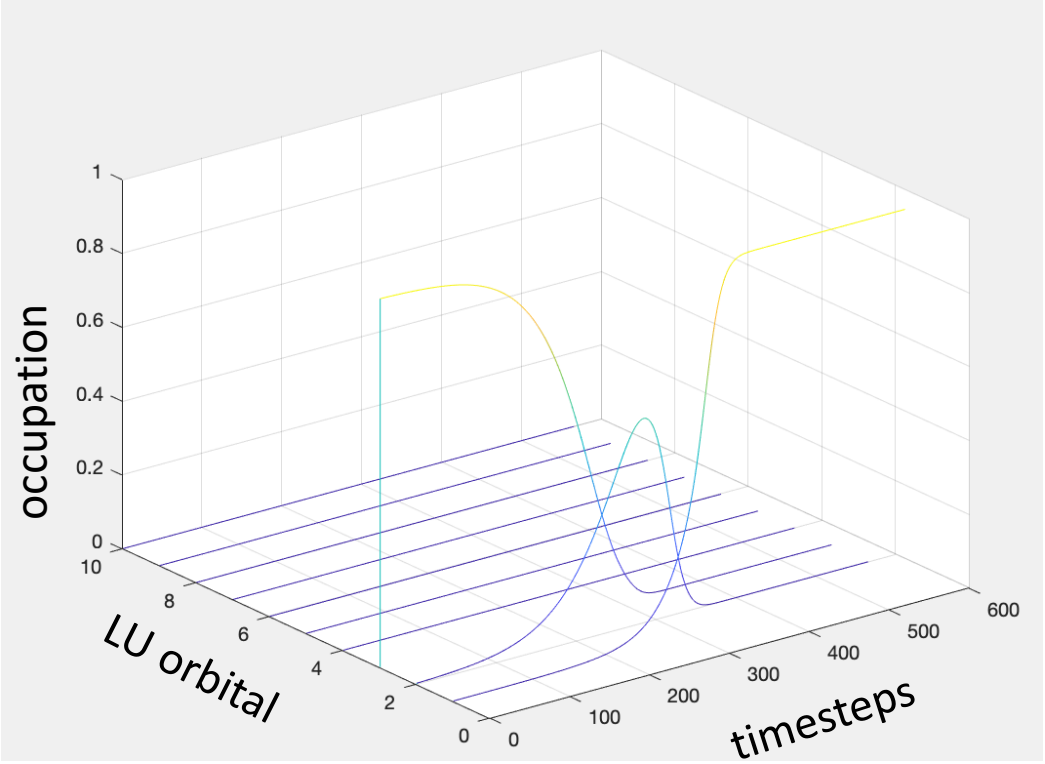
Results of the Electronic Dynamic Calculation

$$P(\varepsilon, t) = \sum_{j \leq HO} \sum_{i \geq LU} \rho_{ii}(t) \cdot \rho_{jj}(t) \delta\left(\varepsilon_i^E - \varepsilon_j^E - \varepsilon\right)$$





Waterfall(PPe)



Waterfall(PPh)

Observables: PLQY, radiative/non-radiative recombination

Joe Granlie

Radiative Recombination

- An excited system will tend to lose energy to return to a minimum energy state. An excited electron can do this by emission of a photon
- The rate of this is given by the Einstein Coefficient for Spontaneous Emission

Nu is the transition energy (E1-E2)

g is degeneracy of state

f is the oscillator strength

Both values can be found from OS_STRENGTH file

$$k_r = A_{ij} = \frac{8\pi^2 \nu_{ij}^2 e^2}{\epsilon_o m_e c^3} \frac{g_j}{g_i} f_{ij}$$

$$f_{ij} = \frac{4\pi m_e \nu_{ij}}{3\hbar e^2} |\vec{D}_{ij}|^2$$

Non-Radiative Recombination

We can use the NACs to calculate the Redfield Tensor, which will tell us the rate of non-radiative recombination

$$V_{ij}^{NAC}(t) = -\frac{i\hbar}{\Delta t}\int \psi_i^*(\vec{r},t)\psi_j(\vec{r},t+\Delta t)d\vec{r}$$

Autocorrelation functions → RRR Matrix → $k_{nr} \approx R_{ij}$

```
>> RRR(18,19)

ans =

   1.0099e-06
```

1/fs

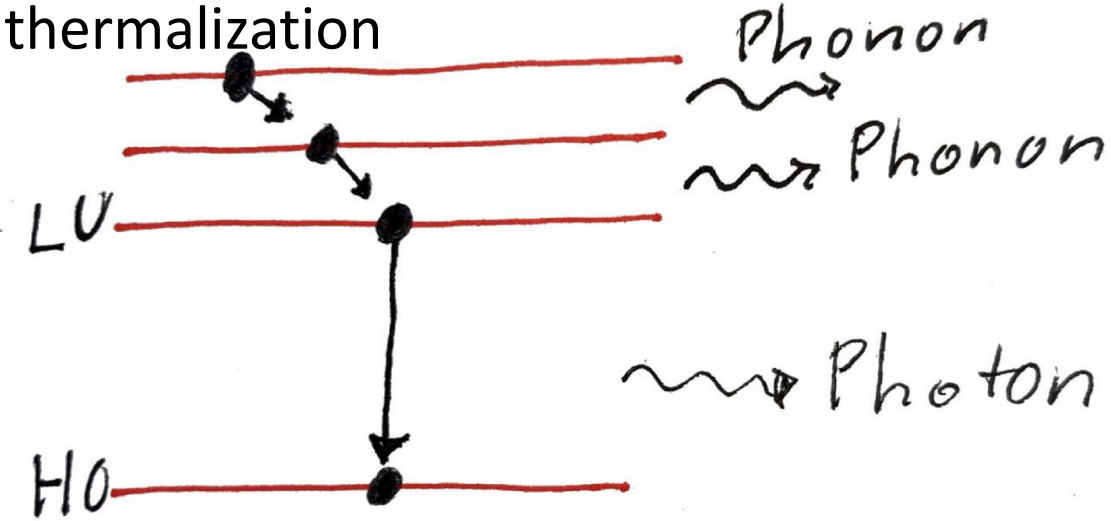
MatLab Script: correlation_v7.m
For HO-LU transition of SiC_CH3_COH model

Photoluminescence Quantum Yield (PLQY)

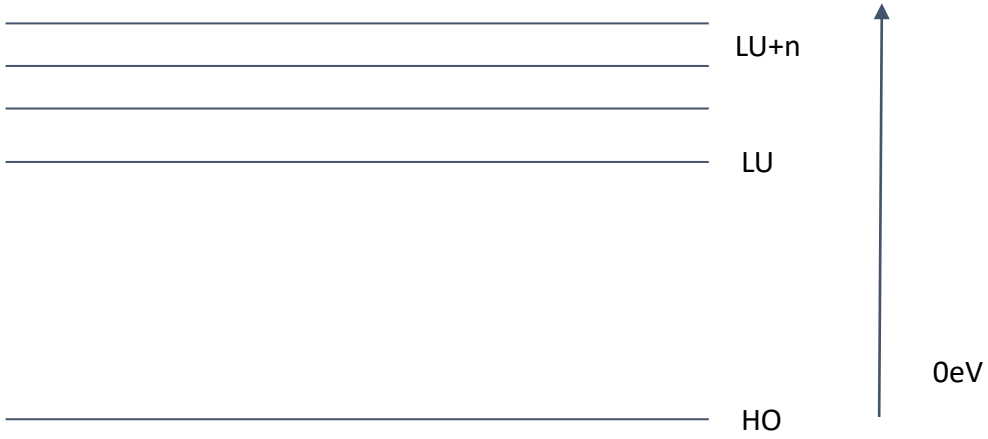
- PLQY tells us the number of photons that are emitted as a fraction of photons absorbed
- Kasha's Rule: highest PLQY is expected to be between HO-LU. Unoccupied orbitals typically have a high overlap → NAC is high → high non-radiative rate in conduction band

$$PLQY = \frac{k_r}{k_r + k_{nr}}$$

Kasha's Rule leads to cascade thermalization



Exceptions to Kasha's Rule



Energy gap for LU and LU+n is high, so they have a lower overlap and thus a lower k_{nr}
Oscillator strength between HO and LU+n is relatively high, so k_r is higher
→ LU+n is in competition with LU for emission

Energy gap is small for HO-LU and HO-LU+n, so large overlap for all excited states
Oscillator strength for HO-LU is low while HO-LU+n is relatively high, so k_r is higher for LU+n
→ LU has a long lifetime