中国科学技术大学
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Spin Related Nonadiabatic Molecular Dynamics by Hefei-NAMD

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OUTLINE

METHODOLOGY

- Time-dependent Schrödinger equation with SOC
- Two representations: spin-adiabatic & spin-diabatic
- Work flow of NAMD with SOC

PRACTICE

- Different calculations of two representations
- VASP patches for outputting SOC matrix elements
- Running NAMD and post data processing

Electronic Time-dependent Schrödinger Equation

The time-dependent Schrödinger equation

$$i\hbar\frac{\partial|\mathbf{\Psi}(\mathbf{r},\mathbf{R}(t),\mathbf{s},t)\rangle}{\partial t} = \hat{\mathcal{H}}^{tot}(\mathbf{r},\mathbf{R}(t),\mathbf{s})|\mathbf{\Psi}(\mathbf{r},\mathbf{R}(t),\mathbf{s},t)\rangle \tag{1}$$

where the total Hamiltonian is given by

$$\hat{\mathcal{H}}^{tot}(\mathbf{r},\mathbf{R}(t),\mathbf{s}) = \hat{\mathcal{H}}^{0}(\mathbf{r},\mathbf{R}(t)) + \hat{\mathcal{H}}^{soc}(\mathbf{r},\mathbf{R}(t),\mathbf{s}) \tag{2}$$

by expanding the wavefunction with a *basis set* $\{|\psi_i\rangle\}$ or *representation*

$$|\mathbf{\Psi}\rangle = \sum_i |\psi_i\rangle\langle\psi_i|\mathbf{\Psi}\rangle = \sum_i c_i|\psi_i\rangle \tag{3}$$

and substituting eq (3) into eq (1), we have

$$\begin{aligned}\frac{\partial c_j(t)}{\partial t} &= -\sum_i \left[i\hbar^{-1}\langle\psi_j|\hat{\mathcal{H}}^{tot}|\psi_i\rangle + \langle\psi_j|\frac{\mathrm{d}}{\mathrm{d}t}|\psi_i\rangle\right]c_i(t) \\ &= -\sum_i \left[i\hbar^{-1}\langle\psi_j|\hat{\mathcal{H}}^{0}|\psi_i\rangle + i\hbar^{-1}\langle\psi_j|\hat{\mathcal{H}}^{soc}|\psi_i\rangle + \langle\psi_j|\frac{\mathrm{d}}{\mathrm{d}t}|\psi_i\rangle\right]c_i(t) \\ &= -\sum_i \left(i\hbar^{-1}H^{0}_{ji} + i\hbar^{-1}H^{soc}_{ji} + T_{ji}\right)c_i(t)\end{aligned} \tag{4}$$

Spin-adiabatic Representation

Expand the wavefunctions in the "*spin-adiabatic* representation"

$$|\Phi\rangle = \sum_n c_n |\psi_n\rangle = \sum_n c_n \begin{pmatrix} |\psi_n^\uparrow\rangle \\ |\psi_n^\downarrow\rangle \end{pmatrix}; \qquad (\hat{\mathcal{H}}^0 + \hat{\mathcal{H}}^{soc})|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

and substitute eq. (10) into TDKS, we have

$$\frac{\partial}{\partial t}\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = -i\hbar^{-1}\begin{pmatrix} \varepsilon_1 & T_{12} & \cdots & T_{1n} \\ T_{21} & \varepsilon_2 & \cdots & T_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ T_{n1} & T_{n2} & \cdots & \varepsilon_n \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix}$$

where

$$T_{ij} = -i\hbar \left(\langle\psi_i^\uparrow| \; \langle\psi_i^\downarrow|\right) \frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} |\psi_j^\uparrow\rangle \\ |\psi_j^\downarrow\rangle \end{pmatrix}$$

- No spin up/down in this case.
- No SOC matrix elements needed, already included in ε_n.
- Straightforward with existing NAMD code.

Spin-diabatic Representation

Expand the wavefunction in the "*spin-diabatic* representation"

$$|\Phi\rangle = \sum_{n\sigma} c_n^\sigma |\psi_n^\sigma\rangle = \sum_n \left[c_n^\uparrow \begin{pmatrix} |\psi_n^\uparrow\rangle \\ 0 \end{pmatrix} + c_n^\downarrow \begin{pmatrix} 0 \\ |\psi_n^\downarrow\rangle \end{pmatrix} \right]; \qquad \hat{\mathcal{H}}^0 |\psi_n^\sigma\rangle = \varepsilon_n^\sigma |\psi_n^\sigma\rangle$$

and substitute eq. (7) into TDKS, we have

$$\frac{\partial}{\partial t}\begin{pmatrix} c_1^\uparrow \\ c_2^\uparrow \\ \vdots \\ c_n^\uparrow \\ c_1^\downarrow \\ c_2^\downarrow \\ \vdots \\ c_n^\downarrow \end{pmatrix} = \frac{-i}{\hbar}\left(\begin{array}{cccc|cccc} \varepsilon_1^\uparrow + S_{11}^{\uparrow\uparrow} & T_{12}^{\uparrow\uparrow} + S_{12}^{\uparrow\uparrow} & \dots & T_{1n}^{\uparrow\uparrow} + S_{1n}^{\uparrow\uparrow} & S_{11}^{\uparrow\downarrow} & S_{12}^{\uparrow\downarrow} & \dots & S_{1n}^{\uparrow\downarrow} \\ T_{21}^{\uparrow\uparrow} + S_{21}^{\uparrow\uparrow} & \varepsilon_2^\uparrow + S_{22}^{\uparrow\uparrow} & \dots & T_{2n}^{\uparrow\uparrow} + S_{2n}^{\uparrow\uparrow} & S_{12}^{\uparrow\downarrow} & S_{22}^{\uparrow\downarrow} & \dots & S_{2n}^{\uparrow\downarrow} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ T_{n1}^{\uparrow\uparrow} + S_{n1}^{\uparrow\uparrow} & T_{n2}^{\uparrow\uparrow} + S_{n2}^{\uparrow\uparrow} & \dots & \varepsilon_n^\uparrow + S_{nn}^{\uparrow\uparrow} & S_{n1}^{\uparrow\downarrow} & S_{n2}^{\uparrow\downarrow} & \dots & S_{nn}^{\uparrow\downarrow} \\ \hline S_{11}^{\downarrow\uparrow} & S_{12}^{\downarrow\uparrow} & \dots & S_{1n}^{\downarrow\uparrow} & \varepsilon_1^\downarrow + S_{11}^{\downarrow\downarrow} & T_{12}^{\downarrow\downarrow} + S_{12}^{\downarrow\downarrow} & \dots & T_{1n}^{\downarrow\downarrow} + S_{1n}^{\downarrow\downarrow} \\ S_{12}^{\downarrow\uparrow} & S_{22}^{\downarrow\uparrow} & \dots & S_{2n}^{\downarrow\uparrow} & T_{21}^{\downarrow\downarrow} + S_{21}^{\downarrow\downarrow} & \varepsilon_2^\downarrow + S_{22}^{\downarrow\downarrow} & \dots & T_{2n}^{\downarrow\downarrow} + S_{2n}^{\downarrow\downarrow} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ S_{n1}^{\downarrow\uparrow} & S_{n2}^{\downarrow\uparrow} & \dots & S_{nn}^{\downarrow\uparrow} & T_{n1}^{\downarrow\downarrow} + S_{n1}^{\downarrow\downarrow} & T_{n2}^{\downarrow\downarrow} + S_{n2}^{\downarrow\downarrow} & \dots & \varepsilon_n^\downarrow + S_{nn}^{\downarrow\downarrow} \end{array}\right)\begin{pmatrix} c_1^\uparrow \\ c_2^\uparrow \\ \vdots \\ c_n^\uparrow \\ c_1^\downarrow \\ c_2^\downarrow \\ \vdots \\ c_n^\downarrow \end{pmatrix}$$

where

$$S_{ij}^{\sigma_1\sigma_2} = \langle\psi_i^{\sigma_1}|\hat{\mathcal{H}}^{soc}|\psi_j^{\sigma_2}\rangle \qquad T_{ij}^{\sigma\sigma} = -i\hbar\langle\psi_i^\sigma|\frac{\mathrm{d}}{\mathrm{d}t}|\psi_j^\sigma\rangle$$

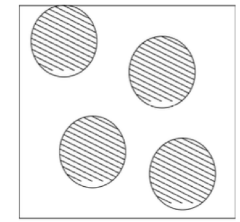
Spin-orbit Couplings in DFT

Spin-orbit Hamiltonian and AE wavefunctions in PAW formalism

$$\hat{\mathcal{H}}^{soc}(\mathbf{r}) = \frac{\hbar\vec{\sigma}\cdot\vec{\mathbf{p}}\times\nabla v_{KS}(\mathbf{r})}{4m^2c^2}; \qquad |\psi_{n\sigma}\rangle = \sum_{i=\{l,m\},\alpha} \langle\tilde{\mathbf{p}}_{i\sigma}|\tilde{\psi}_{n\sigma}\rangle|\phi^{\alpha}_{i\sigma}\rangle$$

Due to the derivatives, SOC is dominated in core region.

AE in PAW sphere



AE

we have

$$\langle\psi_{n_1\sigma_1}|\hat{\mathcal{H}}^{soc}|\psi_{n_2\sigma_2}\rangle = \sum_{\alpha,i,j}\langle\tilde{\psi}_{n_1\sigma_1}|\tilde{\mathbf{p}}^{\alpha}_{i\sigma_1}\rangle\langle\phi^{\alpha}_{i\sigma_1}|\hat{\mathcal{H}}^{soc}|\phi^{\alpha}_{j\sigma_2}\rangle\langle\tilde{\mathbf{p}}^{\alpha}_{j\sigma_2}|\tilde{\psi}_{n_2\sigma_2}\rangle$$

- The projector coefficients $\langle\tilde{\mathbf{p}}_i|\tilde{\psi}_n\rangle$ is contained in `NormalCAR`, which can be easily output and parsed.

$$\langle\phi^{\alpha}_{i\sigma_1}|\hat{\mathcal{H}}^{soc}|\phi^{\alpha}_{j\sigma_2}\rangle = -\frac{1}{2m^2c^2}\langle Y^{\alpha}_i;\sigma_1|\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}|Y^{\alpha}_j;\sigma_2\rangle\langle f^{\alpha}_i|\frac{1}{r}\frac{\mathrm{d}v^{\alpha}_{KS}}{\mathrm{d}r}|f^{\alpha}_j\rangle$$

- This term is *not as easily obtained*, where f^{α}_i is the radial function, Y^{α}_i is the spherical harmonics and KS potential $v^{\alpha}_{KS} = v^{\alpha}_{ext} + v^{\alpha}_{xc} + v^{\alpha}_{Har}$ depend on the charge density of each atom site.

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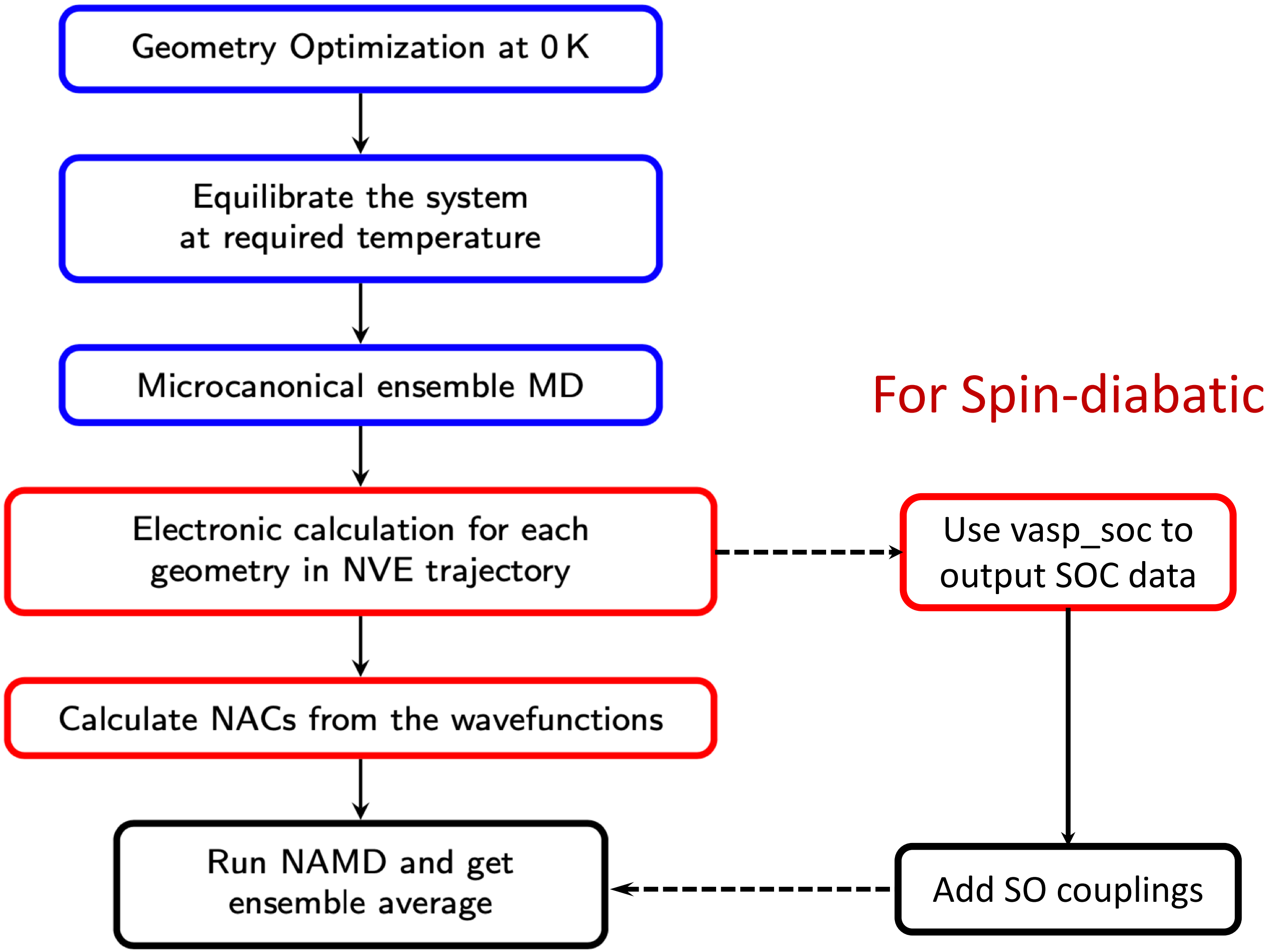
Work Flow



Geometry Optimization at 0 K
Equilibrate the system at required temperature
Microcanonical ensemble MD
For Spin-diabatic
Electronic calculation for each geometry in NVE trajectory
Use vasp_soc to output SOC data
Calculate NACs from the wavefunctions
Run NAMD and get ensemble average
Add SO couplings

Surface Hopping with SOC

Spin-adiabatic Representation

single particle representation

$$\psi_p(\mathbf{r},t) = \sum_j c_j(t)\phi_j(\mathbf{r};\mathbf{R})$$

time-dependent Kohn-Sham equation

$$i\hbar\frac{\partial\psi_p(\mathbf{r},t)}{\partial t} = \mathcal{H}(\mathbf{r};\mathbf{R})\psi_p(\mathbf{r},t)$$

$$i\hbar\dot{c}_j(t) = \sum_k c_k(t)(\varepsilon_k\delta_{jk} - i\hbar d_{jk})$$

$$d_{jk} = \langle\phi_j|\frac{\partial}{\partial t}|\phi_k\rangle$$

FSSH hopping probability

$$P_{jk}(t,\Delta t) = \max\left[\frac{2\int_t^{t+\Delta t}\mathrm{d}t\left[\mathrm{Re}(\rho_{jk}d_{jk})\right]}{\rho_{jj}}, 0\right]$$

Classical-Path Aprroximation

$$G_{jk} = P_{jk}B_{jk}; \quad B_{jk} = \begin{cases}\exp\left\{-\frac{\varepsilon_j-\varepsilon_k}{k_B T}\right\}, & \text{if } \varepsilon_j > \varepsilon_k \\ 1, & \text{if } \varepsilon_j \leqslant \varepsilon_k\end{cases}$$

Surface Hopping with SOC

Spin-diabatic Representation

single particle representation

$$\psi_p(\mathbf{r},t) = \sum_j c_j(t)\phi_j(\mathbf{r};\mathbf{R})$$

time-dependent Kohn-Sham equation

$$i\hbar\frac{\partial\psi_p(\mathbf{r},t)}{\partial t} = \mathcal{H}(\mathbf{r};\mathbf{R})\psi_p(\mathbf{r},t)$$

$$\frac{\partial c_j(t)}{\partial t} = -\sum_i \left(i\hbar^{-1}H^0_{ji} + i\hbar^{-1}H^{soc}_{ji} + T_{ji}\right) c_i(t)$$

$$d_{jk} = \langle\phi_j|\frac{\partial}{\partial t}|\phi_k\rangle$$

The hopping probility within FSSH

$$P_{j\to k}(t,\Delta t) = \max\left(-\frac{2\Delta t\left[\hbar^{-1}\,\mathrm{Im}(c_j^* c_k(H^0_{jk}+H^{soc}_{jk}))-\mathrm{Re}(c_j^* c_k T_{jk})\right]}{c_j^* c_j}, 0\right)$$

Classical-Path Aprroximation

$$G_{jk} = P_{jk}B_{jk};\quad B_{jk} = \begin{cases}\exp\left\{-\frac{\varepsilon_j-\varepsilon_k}{k_B T}\right\}, & \text{if } \varepsilon_j > \varepsilon_k\\ 1, & \text{if } \varepsilon_j \leqslant \varepsilon_k\end{cases}$$

INCARs for Wavefunction Calculations

Spin-adiabatic (vasp_ncl)

```
Electronic Calculation for NAMD
SYSTERM = Ni

#Start Parameter
    ISTART = 0
    ICHARG = 2

#Electronic Relaxation
    ALGO = Fast
    NELM = 100
    PREC = Normal
    ISMEAR = 0
    SIGMA = 0.02
    NPAR = 4

    #ISPIN = 2
    MAGMOM = 0 0 1 0 0 1 0 0 1 0 0 1 0 0 1 0 0 1 0 0
    LSORBIT = .TRUE
    LMAXMIX = 4

#Ionic Relaxation
    IBRION = -1

#Write Flags
    NWRITE = 1
    LREAL = Auto
    LWAVE = .TRUE
    LCHARG = .FALSE
    LORBIT = 11
~
```

Spin-diabatic (vasp_soc)

```
Electronic Calculation for NAMD
SYSTERM = Ni

#Start Parameter
    ISTART = 0
    ICHARG = 2

#Electronic Relaxation
    ALGO = Fast
    NELM = 100
    PREC = Normal
    ISMEAR = 0
    SIGMA = 0.02
    NPAR = 4

    ISPIN = 2
    MAGMOM = 32*1

#Ionic Relaxation
    IBRION = -1

#Write Flags
    NWRITE = 1
    LREAL = Auto
    LWAVE = .TRUE
    LCHARG = .FALSE
    LORBIT = 11
~
~
~
```

VASP Patches

Patches for VASP 5.4.4.

```
zzf@SciNat:Patch_soc$ ls
main.F  paw.F  relativistic.F  stm.F
```

Replace original codes

```
        vasp.5.4.4 (root directory)
                   |
  ---------------------------------------
  |              |          |             |
arch            bin       build          src
                            |             |
                        ---------     ---------
              copy      |    |    |   |           |
       soc  <-------   std  gam  ncl lib        CUDA
```

1. Copy “std” folder to “soc”.
2. Replace original codes by patches.
3. Complile!
4. Copy and rename “vasp” to “vasp_soc”

```
zzf@SciNat:vasp.5.4.4$ ls
arch  build     makefile.include  src
bin   makefile  README
zzf@SciNat:vasp.5.4.4$ cd build/
zzf@SciNat:build$ ls
gam  ncl  std
zzf@SciNat:build$ cp -r std soc
zzf@SciNat:build$ cp /data/zzf/Patch_soc/*.F soc/
zzf@SciNat:build$ cd soc
zzf@SciNat:soc$ make clean
rm -f *.o *.mod *.f90
zzf@SciNat:soc$ make
```

```
zzf@SciNat:soc$ ls vasp
vasp
zzf@SciNat:soc$ cp vasp ../../bin/vasp_soc
zzf@SciNat:soc$ ls ../../bin/
vasp_gam  vasp_ncl  vasp_soc  vasp_std
```

```
NormalCAR  SocCar
```

namd_soc Input Files

inp

```
&NAMDPARA
  BMIN        = 343
  BMAX        = 366
  NBANDS      = 416

  SOCTYPE     = 1 Spin-adiabatic

  NSW         = 2000
  POTIM       = 1
  TEMP        = 300

  NSAMPLE     = 10
  NAMDTIME    = 1000
  NELM        = 1000
  NTRAJ       = 20000
  LHOLE       = .F.

  RUNDIR      = "../run"
  LCPEXT      = .F.
/
```

```
&NAMDPARA
  BMINU       = 168
  BMAXU       = 183
  BMIND       = 149
  BMAXD       = 171
  NBANDS      = 208

  SOCTYPE     = 2 Spin-diabatic

  NSW         = 2000
  POTIM       = 1
  TEMP        = 300

  NSAMPLE     = 10
  NAMDTIME    = 1000
  NELM        = 1000
  NTRAJ       = 20000
  LHOLE       = .F.

  RUNDIR      = "../run"
  LCPEXT      = .F.
/
```

INICON

```
  302   364
  702   366
  689   365
  321   366
  958   366
  316   364
  458   365
  731   366
  254   365
  840   366
```

```
  302   181   1
  702   183   1
  689   183   1
  321   182   1
  958   182   1
  316   183   1
  458   183   1
  731   181   1
  254   183   1
  840   183   1
```

Run NAMD with SOC

Compile namd_soc

```
zzf@SciNat:src$ ls
couplings.f90  lattice.f90  prec.f90     TimeProp.f90
fileio.f90     main.f90     soc.F90      wave.f90
hamil.f90      Makefile     SurfHop.f90
zzf@SciNat:src$ make clean
rm -f *.mod *.a namd
rm -f prec.o lattice.o wave.o fileio.o soc.o couplings.o ha
mil.o TimeProp.o SurfHop.o main.o namd_soc
zzf@SciNat:src$ make
gfortran -g -O2 -c prec.f90
gfortran -g -O2 -c lattice.f90
gfortran -g -O2 -c wave.f90
gfortran -g -O2 -c fileio.f90
gfortran -g -O2 -c soc.F90
gfortran -g -O2 -c couplings.f90
gfortran -g -O2 -c hamil.f90
gfortran -g -O2 -c TimeProp.f90
gfortran -g -O2 -c SurfHop.f90
gfortran -g -O2 -c main.f90
gfortran -g -O2 -o namd_soc prec.o lattice.o wave.o fileio.
o soc.o couplings.o hamil.o TimeProp.o SurfHop.o main.o
zzf@SciNat:src$ cp namd_soc ~/bin
zzf@SciNat:src$
```

NAMD Results

```
zzf@SciNat:namd$ ls
COUPCAR  EIGTXT  INICON  inp  NATXT  PSICT.4  SHPROP.4
zzf@SciNat:namd$
```

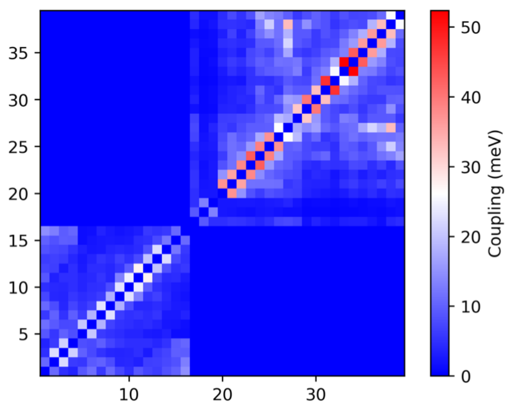
```
zzf@SciNat:namd$ ls
COUPCAR  EIGTXT  INICON  inp  NATXT  PSICT.2  SHPROP.2  SOTXT
zzf@SciNat:namd$
```

```
zzf@SciNat:namd$ namd_soc

 Hefei-NAMD (soc version 1.3.1, Dec 16, 2021)

------------------------------------------------------------
 #../run/01/WAVECAR
 #../run/02/WAVECAR
 #../run/03/WAVECAR
 #../run/04/WAVECAR
 #../run/05/WAVECAR
 #../run/06/WAVECAR
 #../run/07/WAVECAR
 #../run/08/WAVECAR
 #../run/09/WAVECAR
 #../run/10/WAVECAR
 #../run/11/WAVECAR
 #../run/12/WAVECAR
 #../run/13/WAVECAR
 #../run/14/WAVECAR
 #../run/15/WAVECAR
 #../run/16/WAVECAR
 #../run/17/WAVECAR
 #../run/18/WAVECAR
 #../run/19/WAVECAR
 #../run/20/WAVECAR
------------------------------------------------------------
                       BMIN =   316
                       BMAX =   354
                     NBANDS =   416
                    INIBAND =   354
                    SOCTYPE =     1
                        NSW =    21
                      POTIM =   1.0
                       TEMP = 300.0
                   NAMDTINI =     4
                   NAMDTIME =    15
                      NTRAJ = 20000
                       NELM =  1000
                      LHOLE =     F
                       LSHP =     T
                     LCPTXT =     F
                     RUNDIR = ../run
------------------------------------------------------------
CPU Time [s]:    0.27
zzf@SciNat:namd$
```

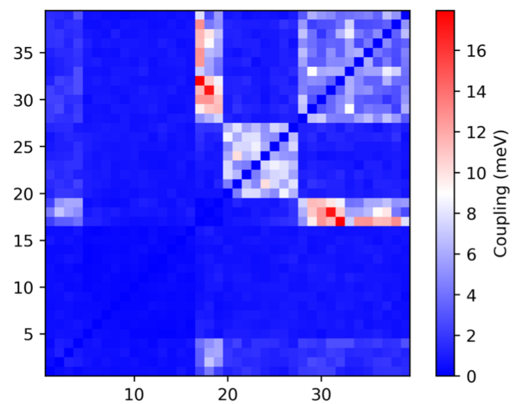
Data Processing After NAMD

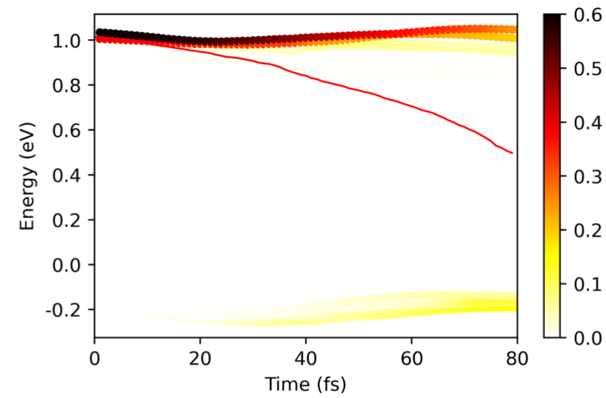
```
zzf@SciNat:namd$ python namdplt.py
zzf@SciNat:namd$ ls *png
COUPLE_NA.png  COUPLE_SO.png  NAMD.png
```

NAC



SOC





More Information

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Hefei-NAMD
https://github.com/QijingZheng/Hefei-NAMD

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往期培训
郑奇靖 | Hefei-NAMD Training Session 2020/12/03
http://staff.ustc.edu.cn/~zqj/posts/Hefei-NAMD-Training/
褚维斌 | Hefei-NAMD 使用的一些经验 2021/05/10
https://www.koushare.com/video/videodetail/11720
蒋翔 | Exciton Dynamics based on Hefei-NAMD 2021/05/10
https://www.koushare.com/video/videodetail/11721

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