

Introduction to Non-Adiabatic Quantum Molecular Dynamics

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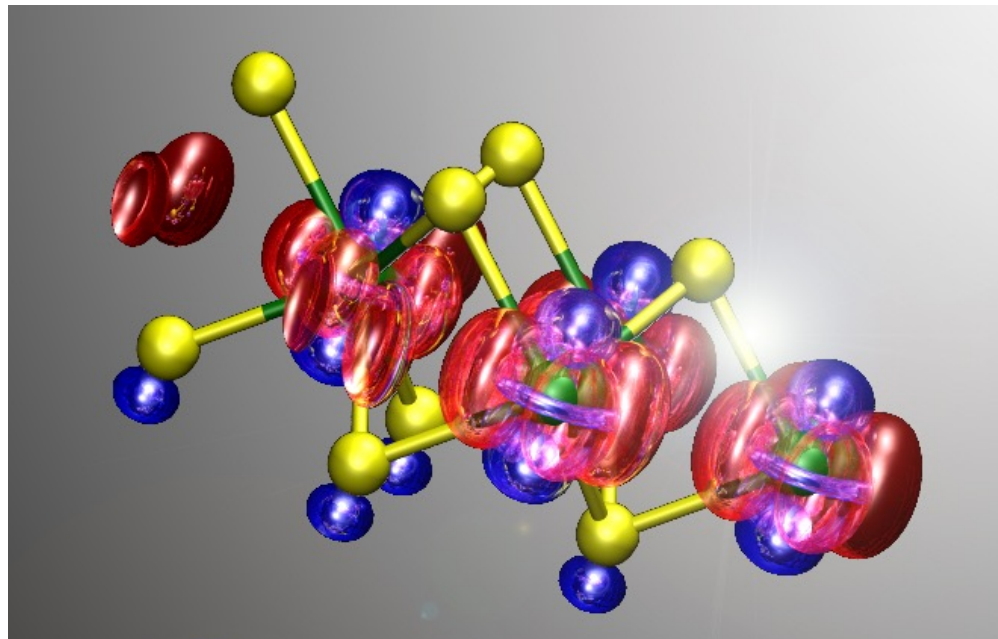
Non-Adiabatic QMD (NAQMD)

Non-Adiabatic QMD (NAQMD):

- Allows electrons to non-radiatively transition between excited states
- Allows for simulation of photo-excitation of materials
- QXMD implements NAQMD based on TDDFT

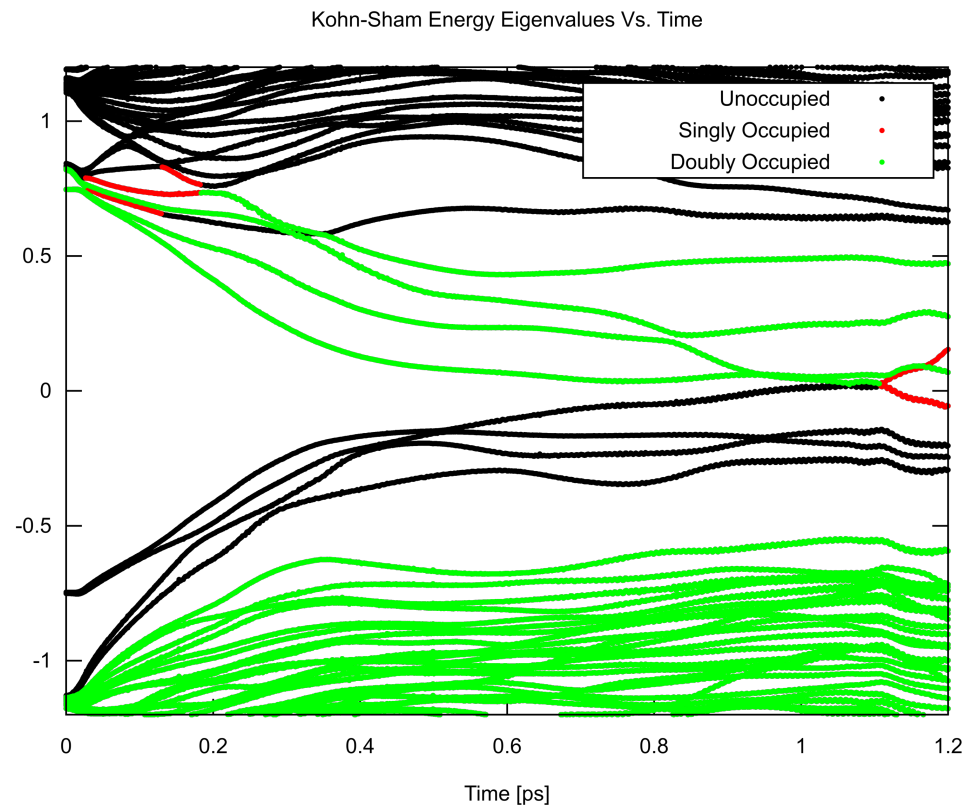
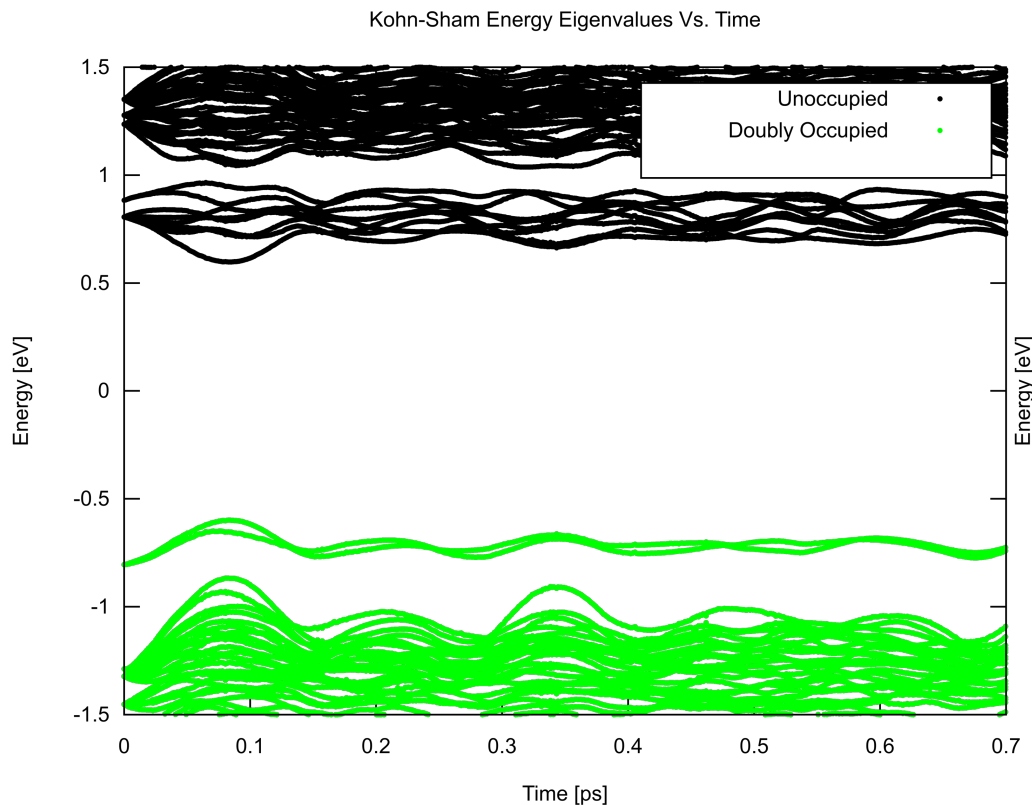
Time-Dependent Density Functional Theory (TDDFT):

- DFT with a time-dependent external potential
- Framework to describe electron dynamics outside of electronic ground state



Adiabatic Vs. Non-Adiabatic QMD

Kohn-Sham energy eigenvalues versus time in adiabatic (left) and non-adiabatic (right) QMD simulations of monolayer MoSe_2 .



Hands-on: Non-Adiabatic Molecular Dynamics

Overview

1. **Execute NAQMD simulation**
2. **Examine input file**
3. **Examine output files**
4. **Post-process and visualize data**

Hands-on: Execute NAQMD Simulation

Goal: Perform NAQMD simulation of monolayer MoSe₂.

1. Check your current directory:

\$ pwd

/staging/magics18/magics##/QXMD_Session/QXMD_HPC/Example/

2. Change to NAQMD/MoSe2 directory

\$ cd 05.NAQMD/MoSe2

\$ls

analysis control data job.pbs

3. Submit NAQMD job

\$ qsub job.pbs



Hands-on: Examine Input File

***TDDFT-MD**

```
(how of it)      :  
  .true.          : (ltddft)  
                  :  
(FSSH-switch)    :  
  .true.          : (lfssh_switch)  
                  :  
(time step)      :  
  0.04d0          : (dttddft)  
                  :  
(restart)         :  
  .false.         : (ltddft_start)  
                  :  
(occupations)    :  
  4               : (nocc_change)  
  35  0.0  0.0    : (numband, occ_new)  
  36  0.0  0.0    :  
  37  2.0  0.0    :  
  38  2.0  0.0    :
```

***end**

Hands-on: Examine Input File

***TDDFT-MD**

(how of it)	:
.true.	: (ltddft)
	:
(FSSH-switch)	:
.true.	: (lfssh_switch)

how of it: True: Run QMD based on TDDFT

False: Run QMD based on DFT

FSSH-switch: True: Allow electrons to hop between bands

False: Electron occupations held fixed

Hands-on: Examine Input File

***TDDFT-MD**

(time step)	:
0.04d0	: (dttdfft)
	:
(restart)	:
.false.	: (ltddft_start)

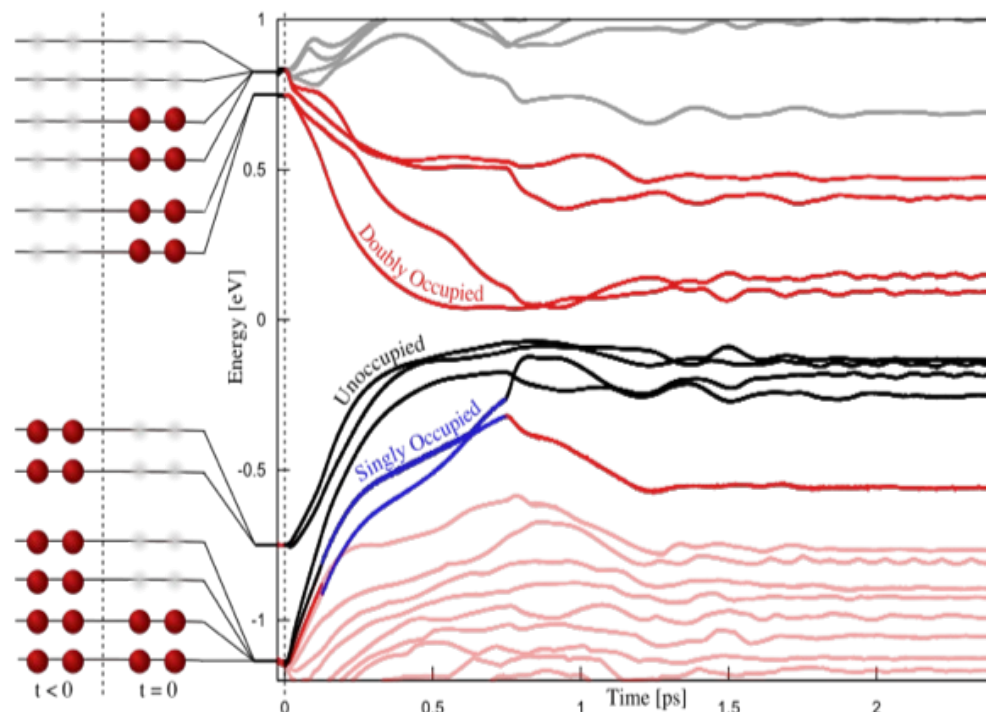
time step: Time step in [a.u.] for numerically integrating TDDFT equations

restart: **True:** Read excited electron occupations from previous run
False: Read electron occupations from input file

Hands-on: Examine Input File

*TDDFT-MD

```
(occupations)      :  
  4                  : (nocc_change)  
 35  0.0  0.0        : (numband, occ_new)  
 36  0.0  0.0        :  
 37  2.0  0.0        :  
 38  2.0  0.0        :
```



occupations: **nocc_change** - # of electronic occupations to be changed
numband - band index of changed occupation
occ_new - new occupations numbers for the given bands
(optionally spin up & spin down)

Hands-on: Examine Input File

```
*dump wavefunctions      :  
(how of it)               :  
  .true.                   : (ldpwav)  
(bands)                   :  
  36, 37                   : (ibstt1,ibstt2)  
(skip step)               :  
  101                      : (nskip_dpwav)  
*end
```

(how of it) – whether or not to dump wavefunction data

(bands) – range of band indices for which to dump wavefunction data

(skip step) – number of steps to skip between dumping data

Hands-on: Examine Output Files

1. Check your current directory:

\$ pwd

/staging/magics18/magics###QXMD_Session/QXMD_HPC/Example/05.NAQMD/MoSe2

2. Change to data/ directory

\$ cd data

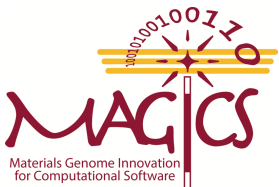
3. New output files of interest:

qm_eigv.d.36.000000 – *3D wavefunction data for band index 36 on the 0th time step*

qm_eigv.d.37.000000 – *3D wavefunction data for band index 37 on the 0th time step*

qm_td_eig.d – *Kohn-Sham eigenenergies of all bands plus band occupancies*

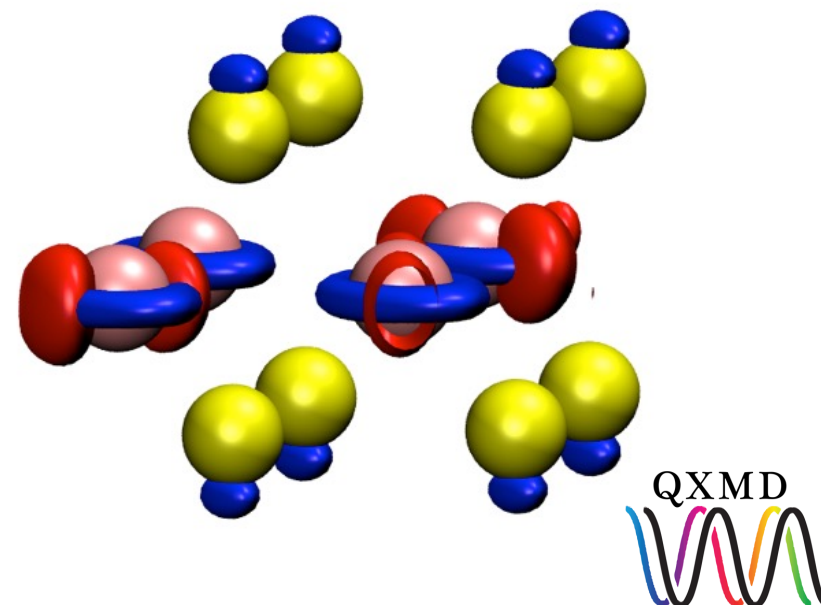
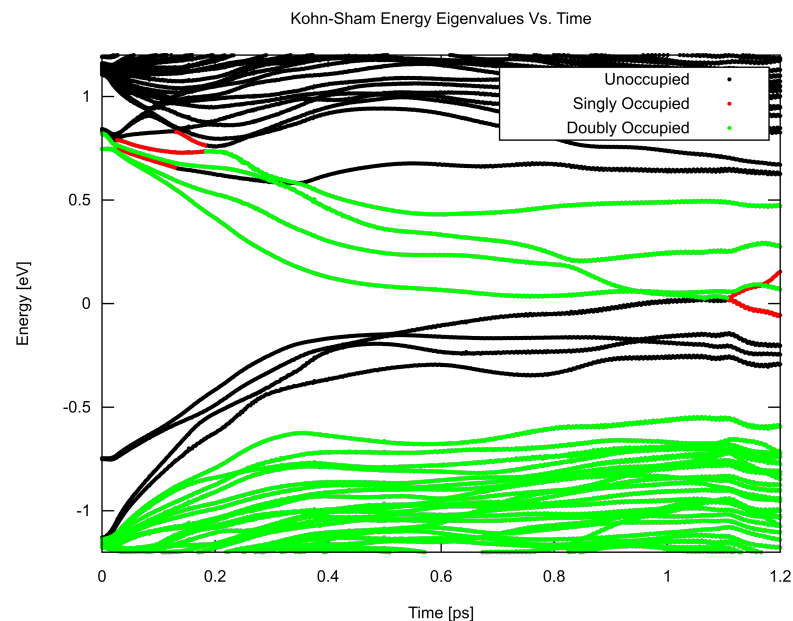
QM_tddftfssh – *Necessary binary file for restarting an NAQMD simulation*



Hands-on: Post-Process Data + Visualization

We will use **utility files** to post-process data and use **gnuplot** and **VMD** to visualize data:

1. A plot of the Kohn-Sham eigenenergies vs. time
 - Run utility file: **eig_exocc.f90**
 - Run **gnuplot script** to create png image



2. Visualize charge densities
 - Run utility file: **gcube.f90**
 - Visualize cube files in **VMD**

Hands-on: Post-Process Data - Eigenenergies

1. Check your current directory:

```
$ pwd
```

```
/staging/magics18/magics###/QXMD_Session/QXMD_HPC/Example/05.NAQMD/MoSe2/data
```

2. Change to analysis/eig directory

```
$ cd ../analysis/eig
```

3. Compile and run utility file for eigenenergies

```
$ifort eig_exocc.f -o eig_exocc
```

```
$./eig_exocc -d ../../data
```

4. Check if post-processing was successful

```
$ls
```

```
EIG.dat eig_exocc eig_exocc.f EIG_occ-one.dat EIG_occ-two.dat plot_eig.gnu
```



Hands-on: Visualize Data - Eigenenergies

1. Check your current directory:

\$ pwd

/staging/magics18/magics###/QXMD_Session/QXMD_HPC/Example/05.NAQMD/MoSe2/analysis/eig

2. Run gnuplot script

\$ gnuplot plot_eig.gnu

3. Check if plotting was successful

\$ls

EIG.dat eig.png eig_exocc eig_exocc.f EIG_occ-one.dat EIG_occ-two.dat plot_eig.gnu

4. Copy 'eig.png' to your local computer to view!

- Use scp or filezilla

Filezilla

hpc-login3.usc.edu magicsXX Password

Host: sftp://hpc-login3.us Username: sctiwari Password: Quick connect

Status: Retrieving directory listing of "/staging/pv/sctiwari/workshop/QXMD_HPC/Examples/01.Optimization/H2O/analysis/PDB"...
Status: Listing directory /staging/pv/sctiwari/workshop/QXMD_HPC/Examples/01.Optimization/H2O/analysis/PDB
Status: Directory listing of "/staging/pv/sctiwari/workshop/QXMD_HPC/Examples/01.Optimization/H2O/analysis/PDB" successful
Status: Connecting to hpc-login3.usc.edu...
Status: Connected to hpc-login3.usc.edu
Status: Starting download of /staging/pv/sctiwari/workshop/QXMD_HPC/Examples/01.Optimization/H2O/analysis/PDB/config.pdb
Status: File transfer successful, transferred 4,355 bytes in 1 second

Local site: /Users/sctiwari/Downloads/QXMD_HPC/ Remote site: /staging/pv/sctiwari/workshop/QXMD_HPC/Examples/01.Optimization/H2O/analysis/PDB

Local Computer

Filename	Filesize	Filetype	Last modified
..		Directory	03/01/2018 00:4...
Examples		Directory	02/28/2018 20:...
Lib		Directory	02/28/2018 20:...
Program		Directory	03/01/2018 00:4...
util		Directory	03/01/2018 00:4...
.DS_Store	6,148	File	03/01/2018 01:0...
config.pdb	4,355	CrystalMaker...	03/01/2018 11:0...

2 files and 4 directories. Total size: 10,503 bytes

Remote Computer

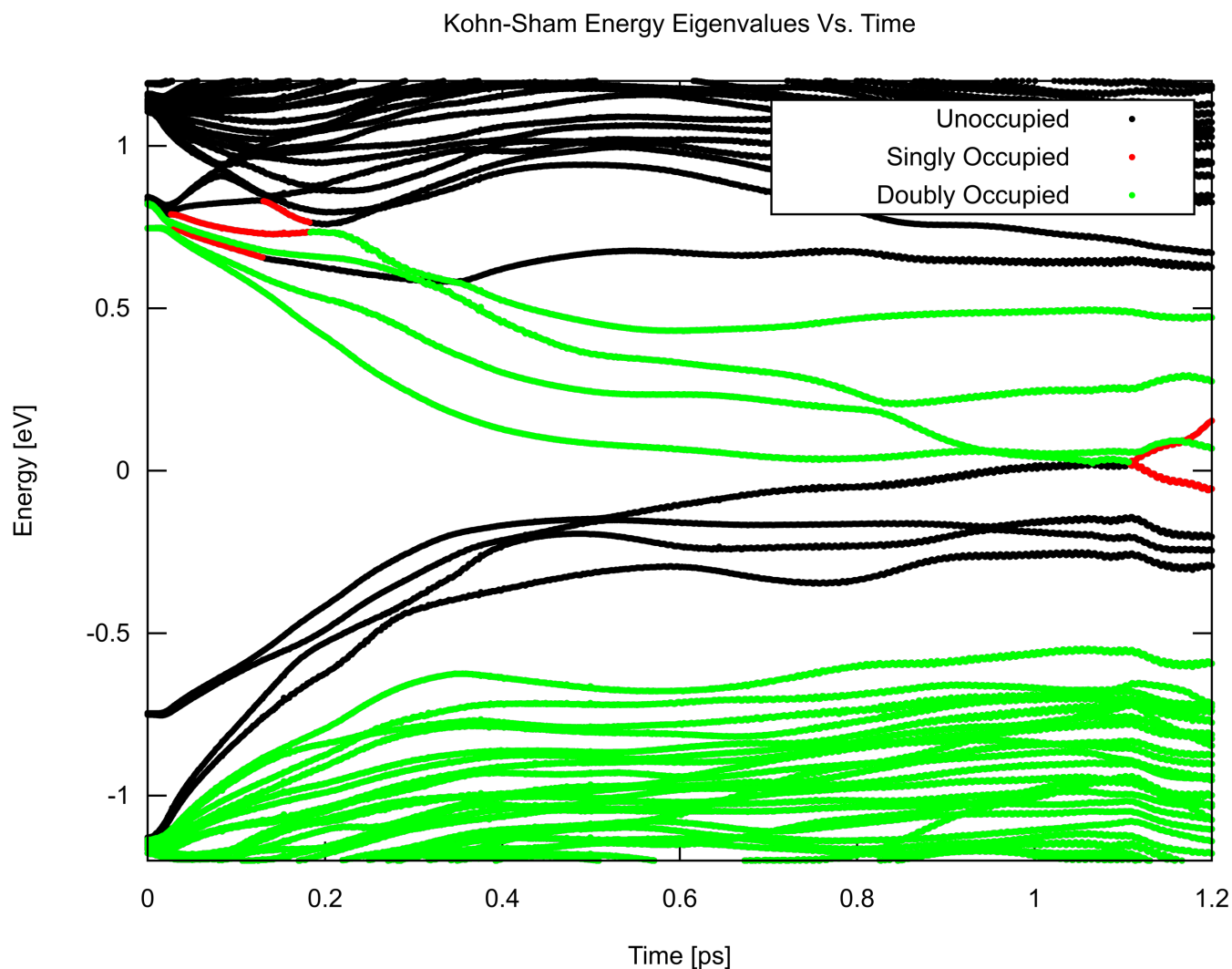
Filename	Filesize	Filetype	Last modified	Permissions	Owner/Group
..		Directory	03/01/2018 00:...	-rwxr-xr-x	sctiwari c...
a.out	944,928	out file	03/01/2018 00:...	-rw-r--r--	sctiwari c...
config.pdb	4,355	File	03/01/2018 11:...	-rw-r--r--	sctiwari c...
toPDBcell	944,928	File	03/01/2018 00:...	-rwxr-xr-x	sctiwari c...
toPDBcell.f	8,030	f-file	02/28/2018 ...	-rw-r--r--	sctiwari lc...

Selected 1 file. Total size: 4,355 bytes

Server/Local file Direction Remote file Size Priority Status

Hands-on: Visualize Data - Eigenenergies

Energies and occupations of the electronic bands, as a function of time, after simulating photoexcitation a 2x2x1 supercell of monolayer MoSe₂.



Hands-on: Post-Process Data – Charge Density

1. Check your current directory:

```
$ pwd
```

```
/staging/magics18/magics###/QXMD_Session/QXMD_HPC/Example/05.NAQMD/MoSe2/analysis/eig
```

2. Change to analysis/GCube directory

```
$ cd ../GCube
```

```
$ ls
```

```
gcube.f90
```

3. Compile and run utility file for wavefunctions

```
$ifort gcube.f90 -o gcube
```

```
$/gcube -d ../../data -n 101 -ib 36 -eb 37
```

4. Check if post-processing was successful

```
$ls
```

```
gcube  gcube.f90
```

```
state.36.000000.cube  state.37.000000.cube
```

5. Copy cube files to your local computer for visualization!

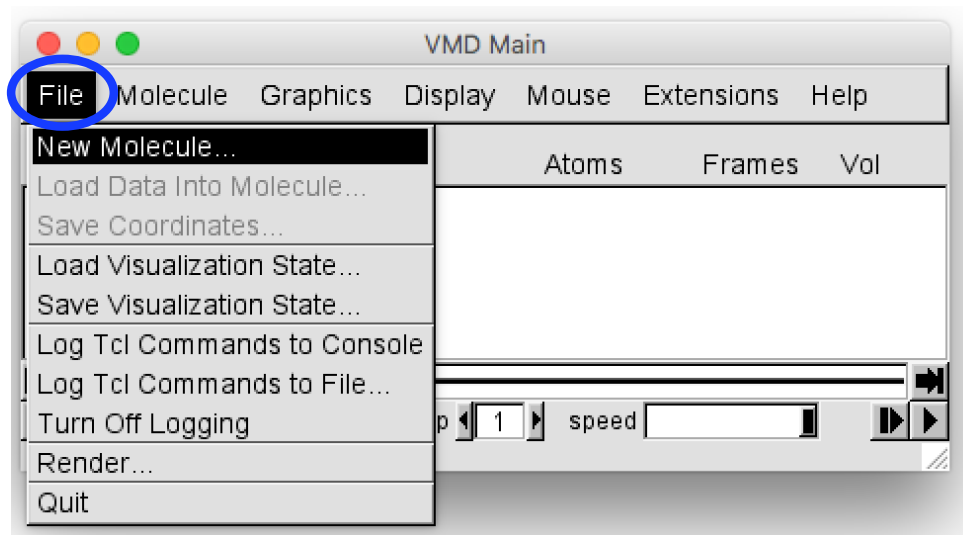


Hands-on: Visualization – Charge Density

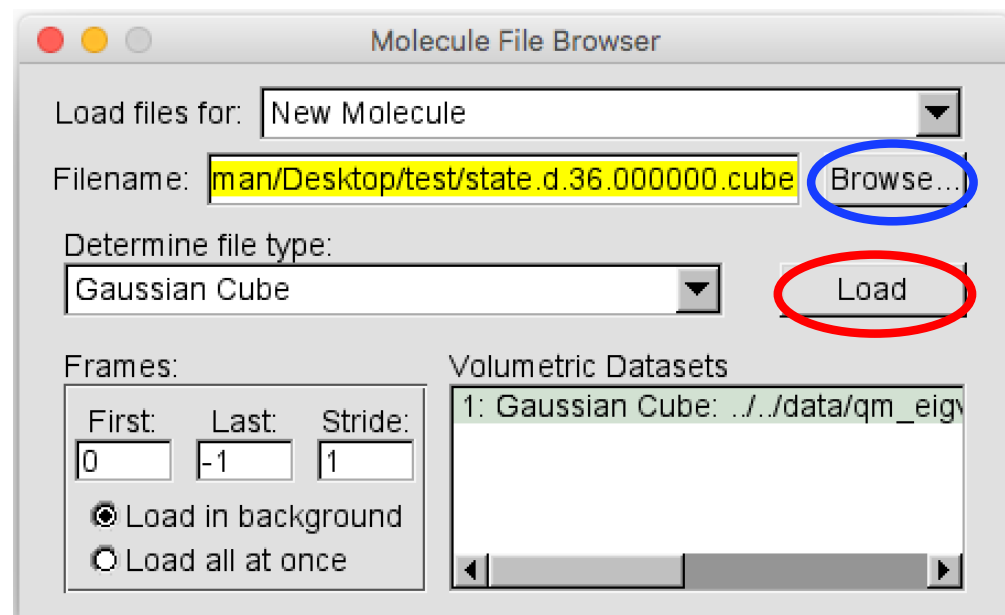
Load HOMO charge density
(Highest Occupied Molecular Orbital)

Open VMD

File -> New Molecule



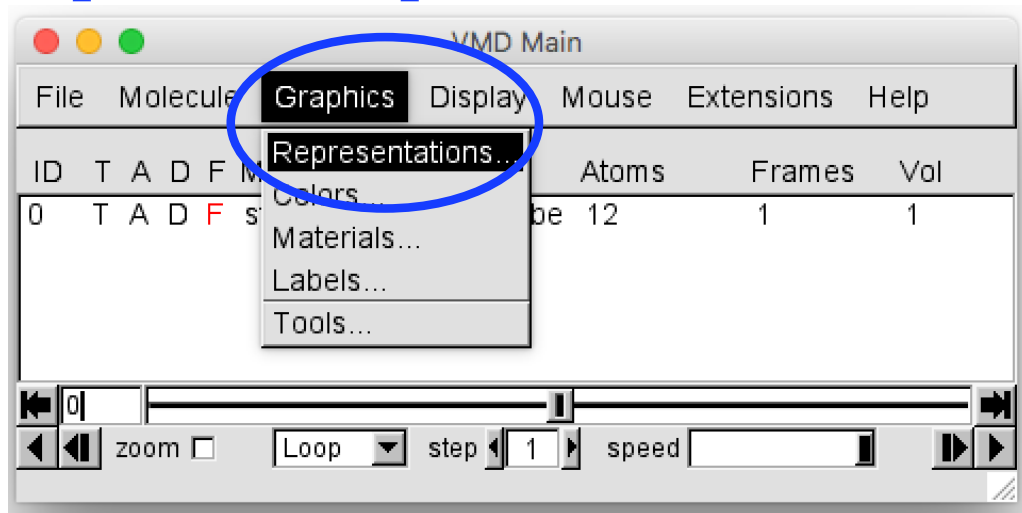
Browse -> select/path/to/state.36.000000.cube



Click Load

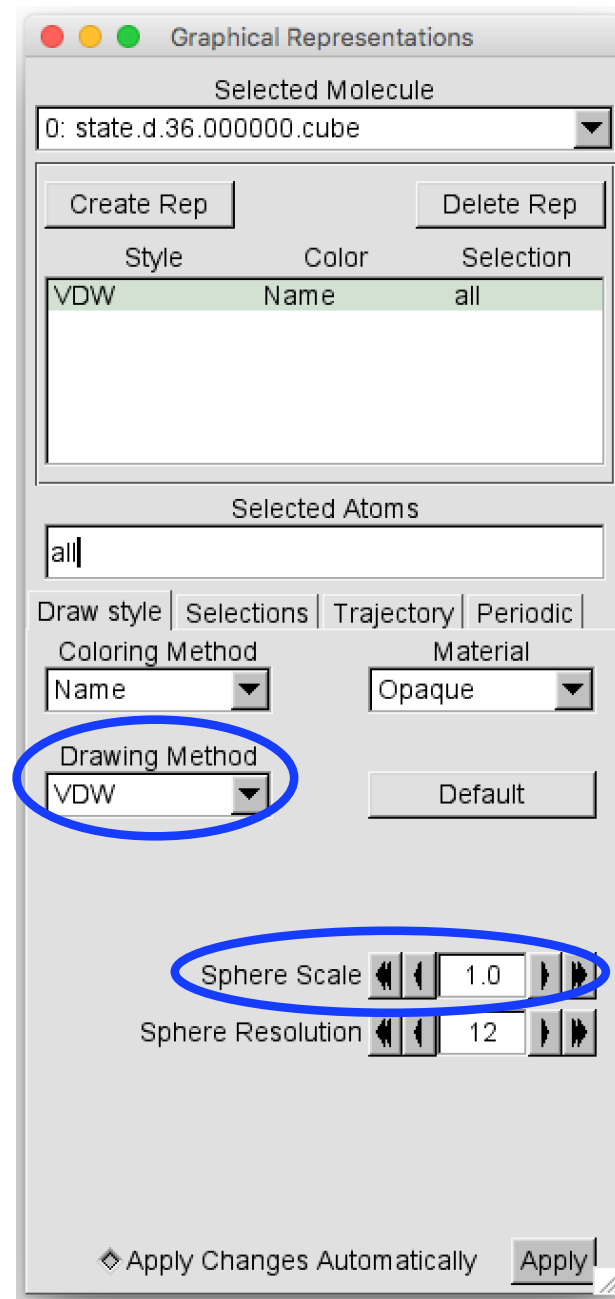
Hands-on: Visualization - Charge Density

Graphics -> Representations



Drawing Method: VDW

Sphere Scale: 0.3



Hands-on: Visualization - Charge Density

Graphics -> Representations

Click Create Rep

Set **Coloring Method**: ColorID, 0 (Blue)

Set **Drawing Method**: Isosurface

Set **Isovalue**: your choice!

Set **Draw**: Solid Surface

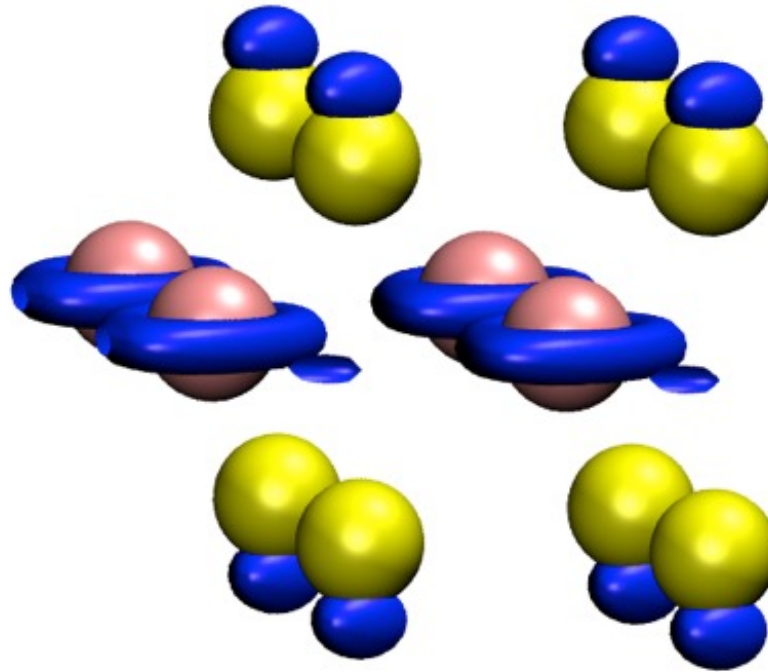
Set **Show**: Isosurface

The screenshot shows the 'Graphical Representations' dialog box. The 'Selected Molecule' dropdown is set to '0: state.d.36.000000.cube'. The 'Create Rep' button is circled in red. Below it, a table lists representations:

Style	Color	Selection
VDW	Name	all
Isosurface	ColorID 0	<volume>

The 'Selected Atoms' dropdown is set to 'all'. The 'Draw style' tab is selected. The 'Coloring Method' dropdown is set to 'ColorID' and the 'ColorID' dropdown is set to '0'. The 'Material' dropdown is set to 'Opaque'. The 'Drawing Method' dropdown is set to 'Isosurface'. The 'Range' is set to '67078' and '12813'. The 'Vol' dropdown is set to 'vol0: state.d.36'. The 'Isovalue' is set to '-0.043374'. The 'Step' is set to '1' and the 'Size' is set to '1'. The 'Draw' dropdown is set to 'Solid Surface' and the 'Show' dropdown is set to 'Isosurface'. The 'Apply Changes Automatically' checkbox is checked and the 'Apply' button is visible.

Hands-on: Visualization - Charge Density

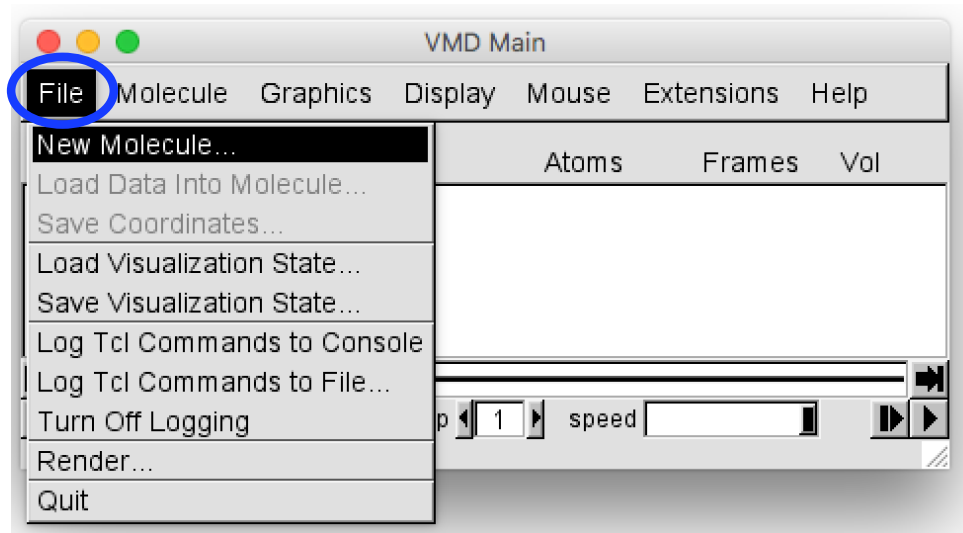


Hands-on: Visualization – Charge Density

Load LUMO charge density
(Lowest Unoccupied Molecular Orbital)

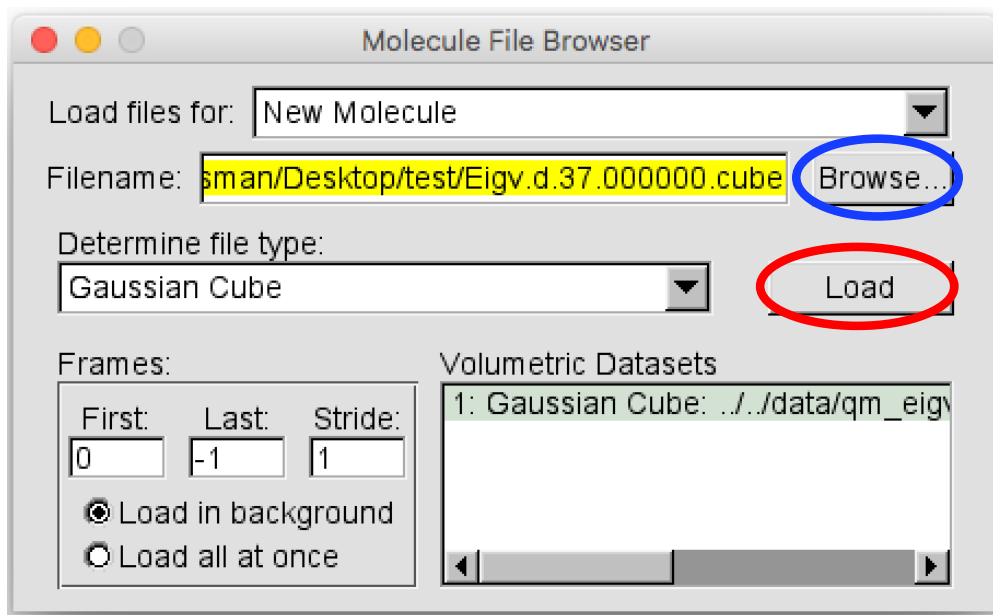
Open VMD

File -> New Molecule



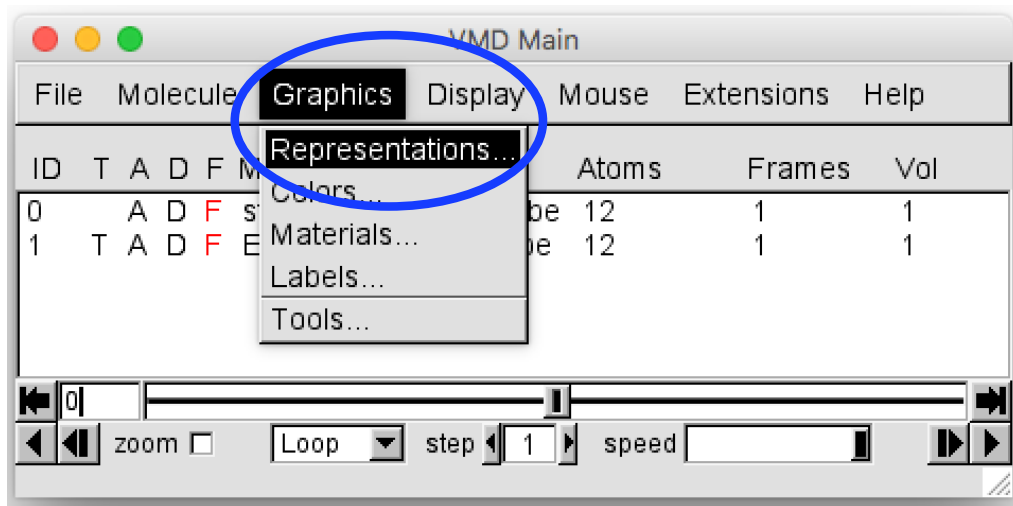
Browse -> select/path/to/state.37.000000.cube

Click Load



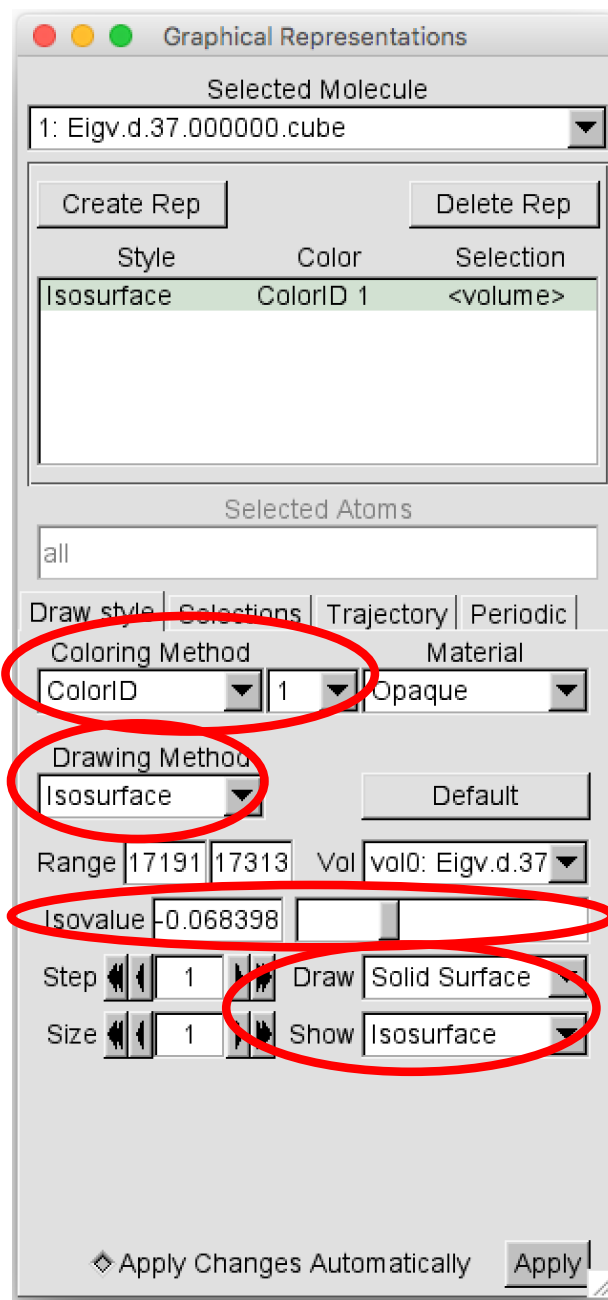
Hands-on: Visualization - Charge Density

Graphics -> Representations



Hands-on: Visualization - Charge Density

Graphics -> Representations



Set **Coloring Method**: ColorID, 1 (Red)

Set **Drawing Method**: Isosurface

Set **Isovalue**: your choice!

Set **Draw**: Solid Surface

Set **Show**: Isosurface

Hands-on: Visualization - Charge Density

