

# Introduction to Non-Adiabatic Quantum Molecular Dynamics

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**Lindsay Bassman**

**Hiroyuki Kumazoe, Aravind Krishnamoorthy, Subodh Tiwari**

*Collaboratory for Advanced Computing and Simulation*

*Department of Material Science & Department of Physics*

*University of Southern California*



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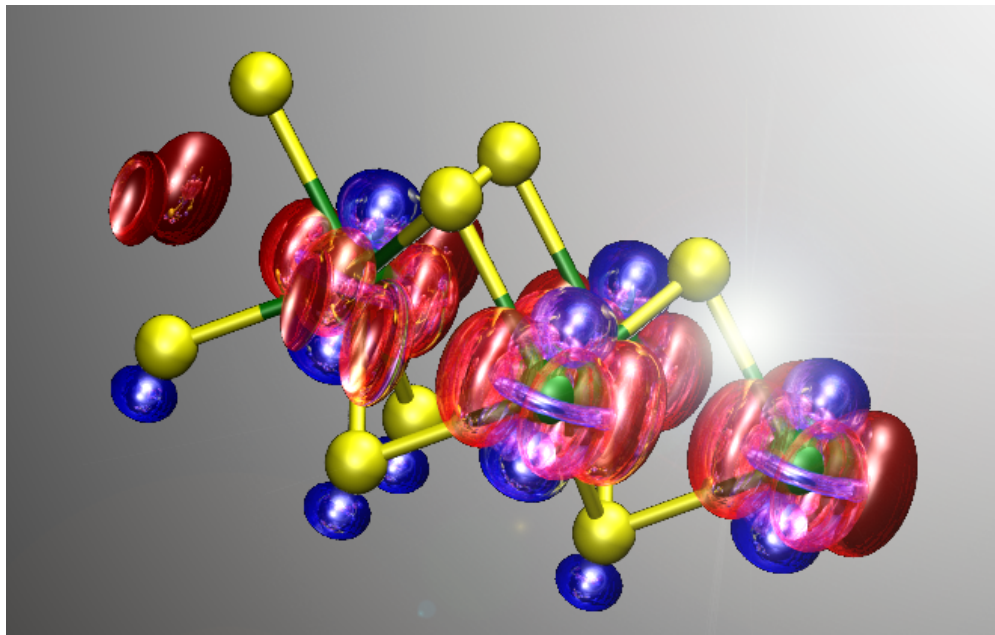
# Non-Adiabatic QMD (NAQMD)

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):

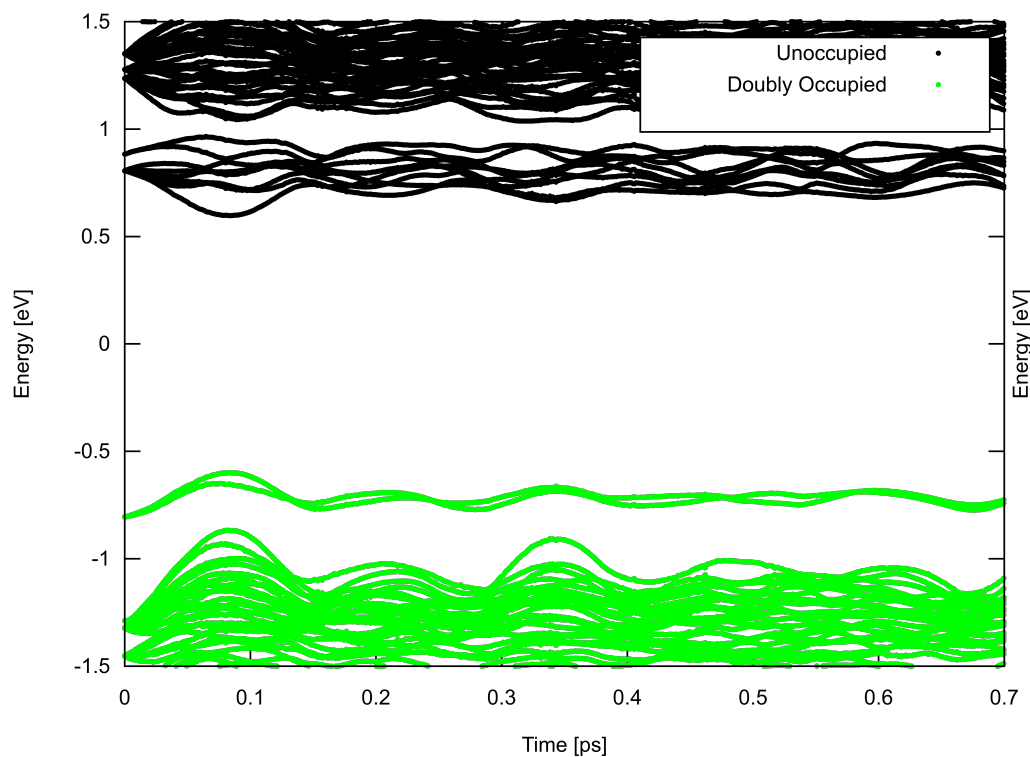
- DFT with a time-dependent external potential
- Framework to describe electron dynamics outside of electronic ground state



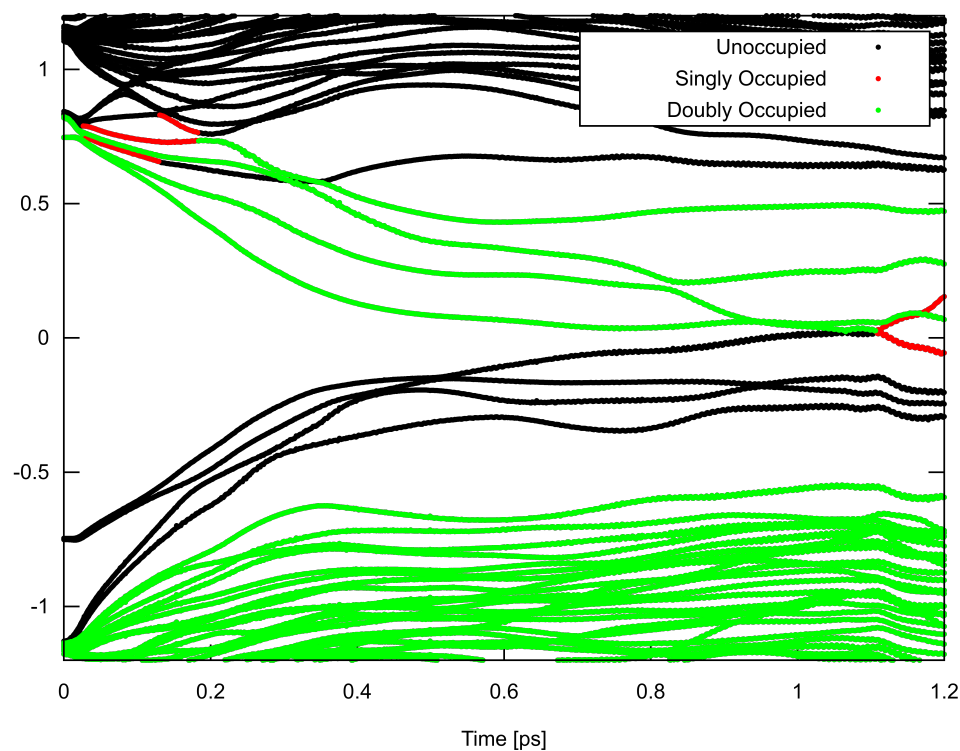
# Adiabatic Vs. Non-Adiabatic QMD

Kohn-Sham energy eigenvalues versus time in adiabatic (left) and non-adiabatic (right) QMD simulations of monolayer  $\text{MoSe}_2$ .

Kohn-Sham Energy Eigenvalues Vs. Time



Kohn-Sham Energy Eigenvalues Vs. Time



# Hands-on: Non-Adiabatic Molecular Dynamics

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## Overview

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

# Hands-on: Execute NAQMD Simulation

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**Goal: Perform NAQMD simulation of monolayer MoSe<sub>2</sub>.**

**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         : (dtddft)  
                :  
(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	: (dtddft)
	:
(restart)	:
.false.	: (ltddft_start)

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

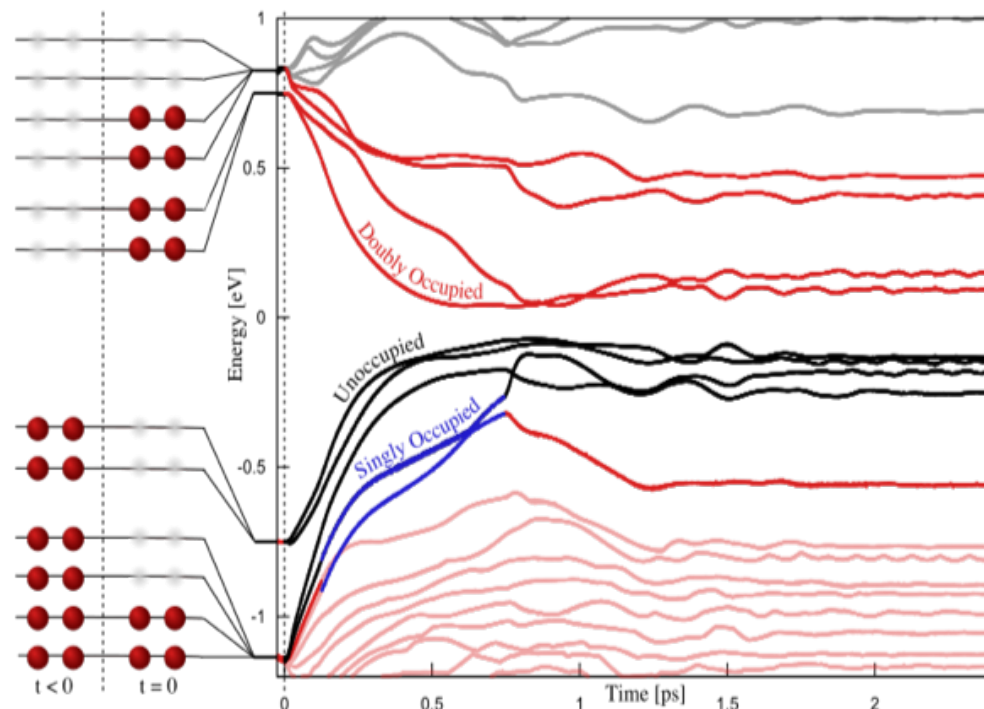
**restart:** **True:** Read excited electron occupations from previous run  
**False:** Read electron occupations from input file



# 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

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## 1. Check your current directory:

**\$ pwd**

**/staging/magics18/magics###/QXMD\_Session/QXMD\_HPC/Example/05.NAQMD/MoSe2**

## 2. Change to data/ directory

**\$ cd data**

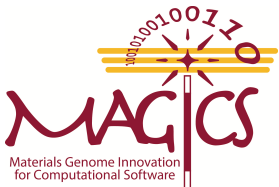
## 3. New output files of interest:

**qm\_eigv.d.36.000000** – *3D wavefunction data for band index 36 on the 0<sup>th</sup> time step*

**qm\_eigv.d.37.000000** – *3D wavefunction data for band index 37 on the 0<sup>th</sup> 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: Examine Output Files

qm\_td\_eig.d

Eigenvalues of GS & occupations of Excited States

Time Step	0	37	48	Total # of bands
1	-1.05134E+00	2.000		
2	-9.88806E-01	2.000		
3	-9.20127E-01	2.000		
4	-9.20098E-01	2.000		
5	-9.20069E-01	2.000		
6	-9.06340E-01	2.000		
7	-9.06318E-01	2.000		
8	-9.06282E-01	2.000		
9	-4.25270E-01	2.000		
10	-4.25228E-01	2.000		
	.			
	.			
	.			
32	-6.01210E-02	2.000		
33	-4.53140E-02	2.000		
34	-4.52551E-02	2.000		
35	-4.52010E-02	0.000		
36	-3.20278E-02	0.000		
37	1.32496E-01	2.000		
38	1.32551E-01	2.000		
39	1.32570E-01	0.000		
40	1.66741E-01	0.000		
41	1.66840E-01	0.000		
42	1.66905E-01	0.000		
43	2.10103E-01	0.000		
44	2.10188E-01	0.000		
45	2.19202E-01	0.000		
46	2.19309E-01	0.000		
47	2.49565E-01	0.000		
48	2.57675E-01	0.000		

Band Indices

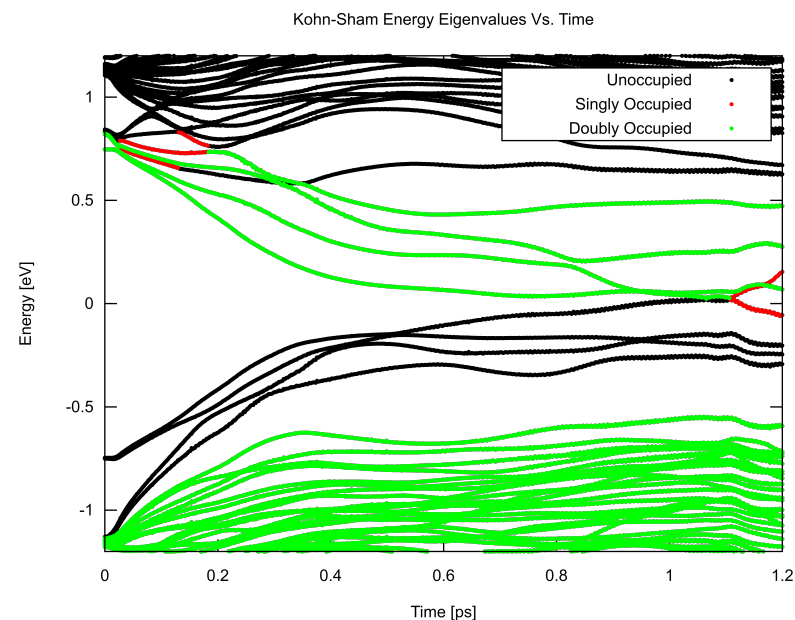
Energy Eigenvalues (Ry)

Band Occupation Number

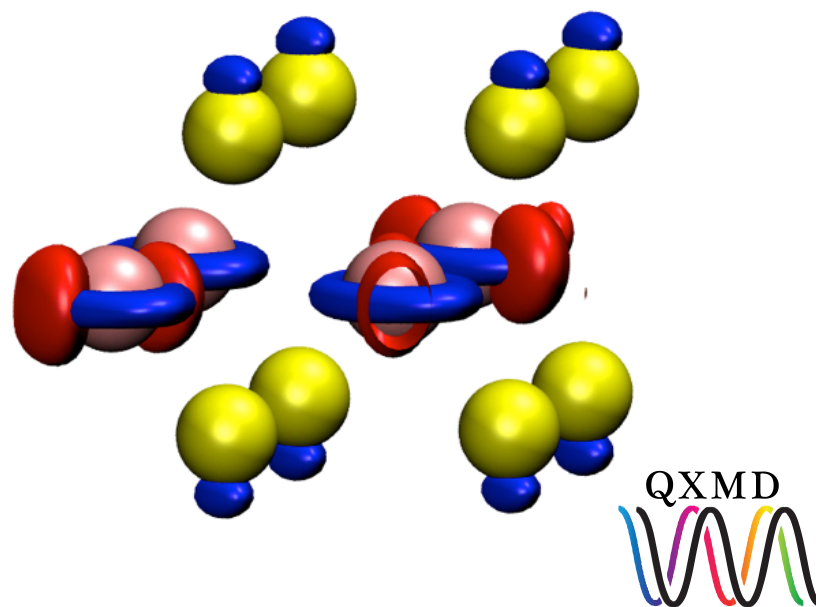
# Hands-on: Post-Process Data + Visualization

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

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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

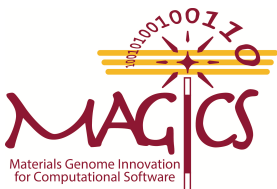
**\$ifort eig\_exocc.f -o eig\_exocc**

**\$/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

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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**

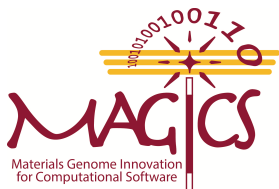
3. Check if plotting was successful

**\$ 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

sftp://sctiwari@hpc-login3.usc.edu - FileZilla

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/analy

Local site files:

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...

Remote site files:

Filename	Filesize	Filetype	Last modified	Permissions	Owner/Group
..		Directory			
a.out	944,928	out file	02/01/2018 0...	-rwxr-xr-x	sctiwari c...
config.pdb	4,355	Crystal...	03/01/2018 1...	-rw-r--r--	sctiwari c...
toPDBcell	944,928	File	03/01/2018 0...	-rwxr-xr-x	sctiwari c...
toPDBcell.f	8,030	f-file	02/28/2018 ...	-rw-r--r--	sctiwari lc...

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

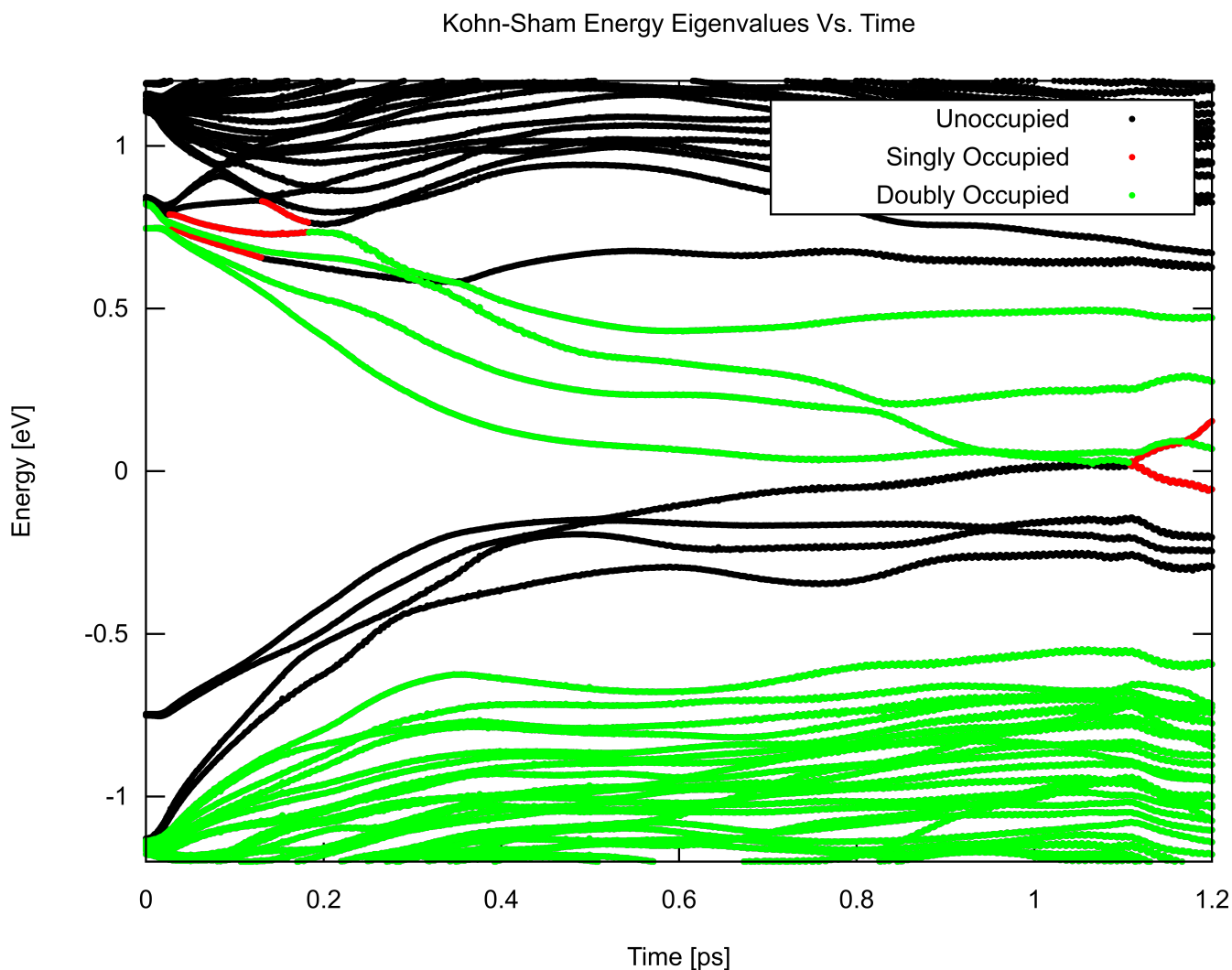
Selected 1 file. Total size: 4,355 bytes

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 MoSe<sub>2</sub>.



# Hands-on: Post-Process Data – Charge Density

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## 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
```

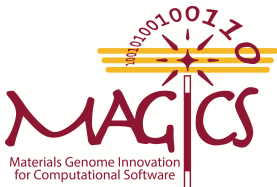
```
$/gcube -d ../../data -n 101 -ib 36 -eb 37
```

## 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

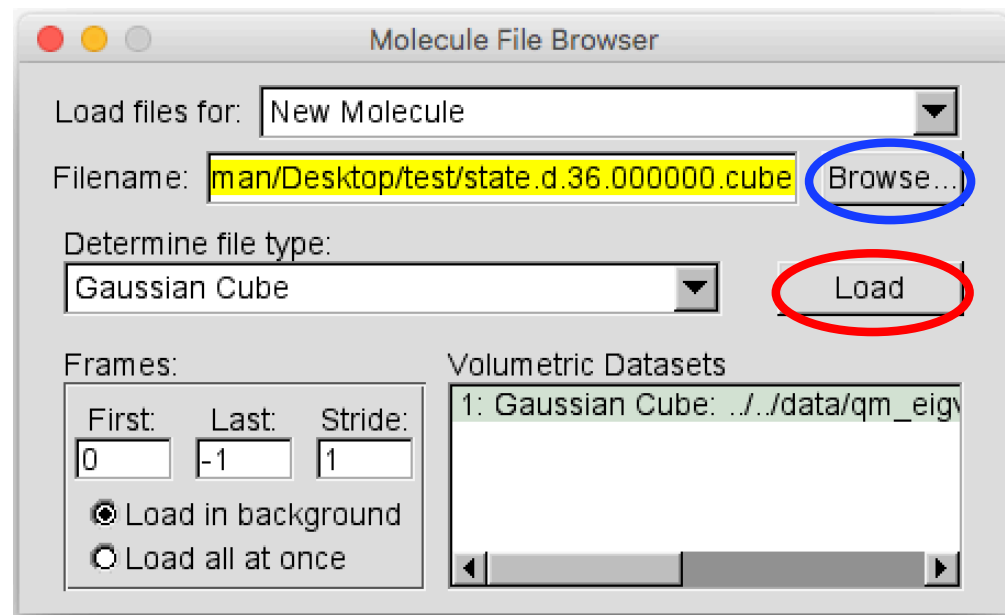
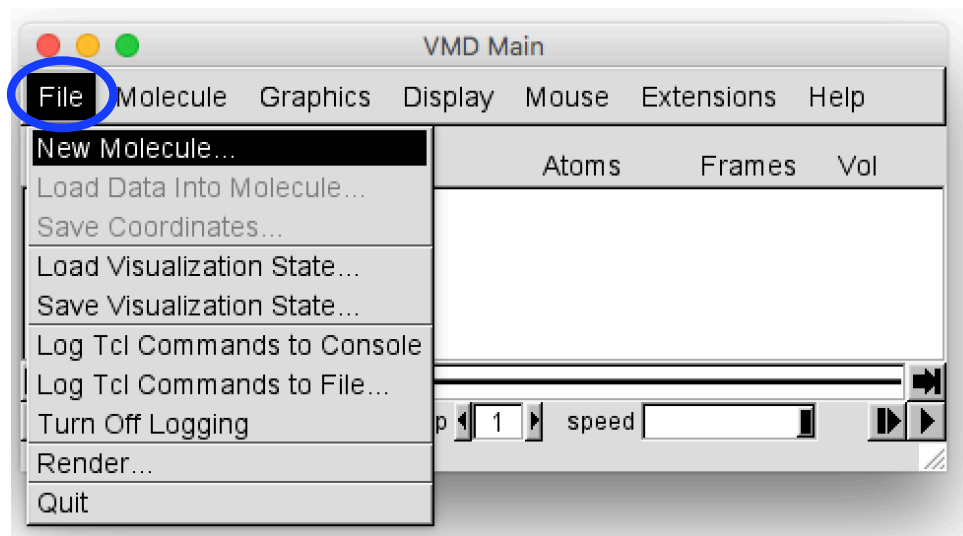
**Load HOMO charge density**  
(Highest Occupied Molecular Orbital)

**Open VMD**

**File -> New Molecule**

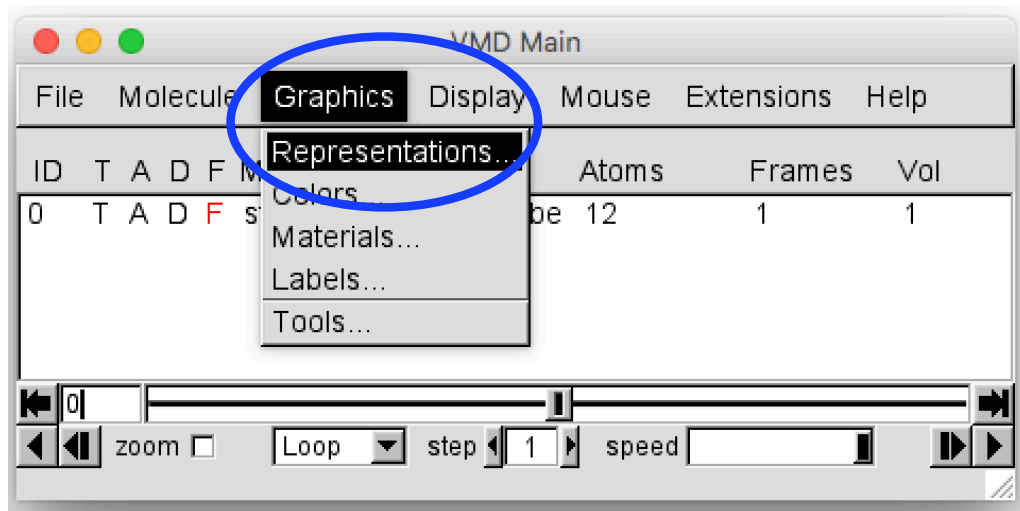
**Browse -> select/path/to/state.36.000000.cube**

**Click Load**



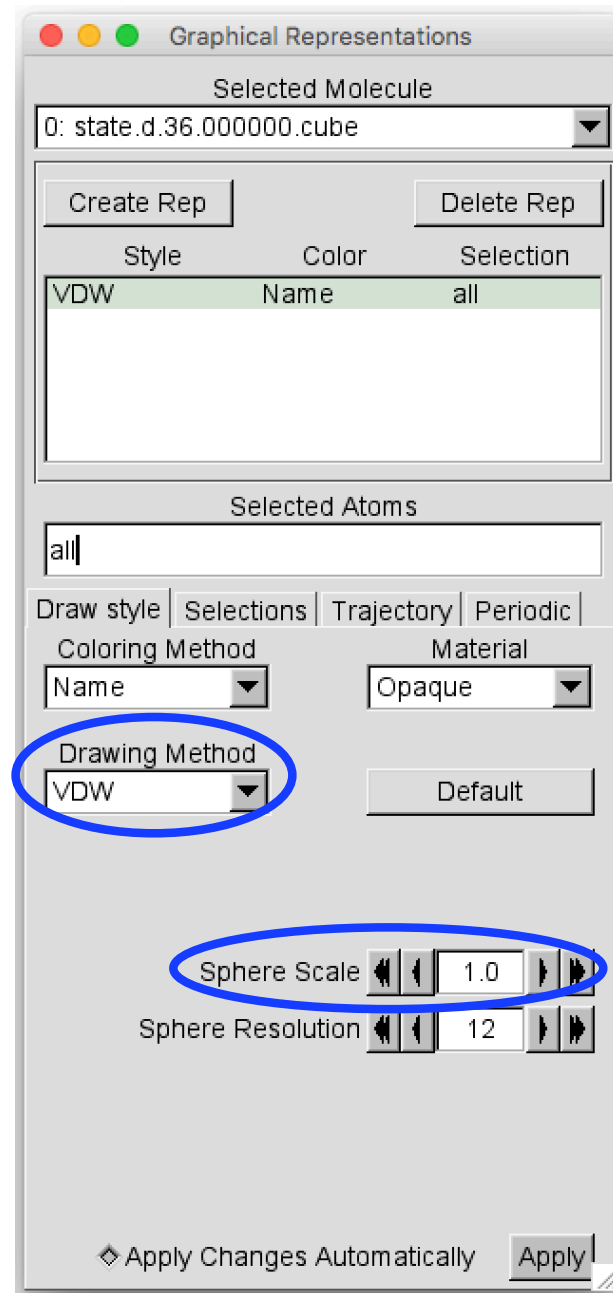
# Hands-on: Visualization - Charge Density

## 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

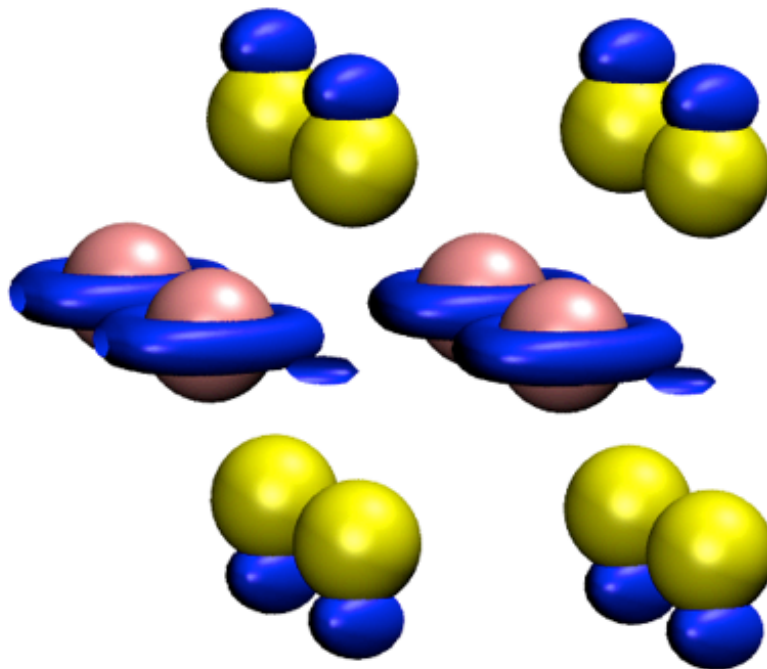
The screenshot shows the 'Graphical Representations' dialog box. The 'Selected Molecule' dropdown is set to '0: state.d.36.000000.cube'. The 'Create Rep' button is circled in red. Below it, a table lists representations:

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 'Drawing Method' dropdown is set to 'Isosurface'. The 'Range' is set to '67078' and '12813'. The 'Isovalue' is set to '-0.043374'. The 'Draw' dropdown is set to 'Solid Surface' and the 'Show' dropdown is set to 'Isosurface'. The 'Apply' button is at the bottom right.

# Hands-on: Visualization - Charge Density

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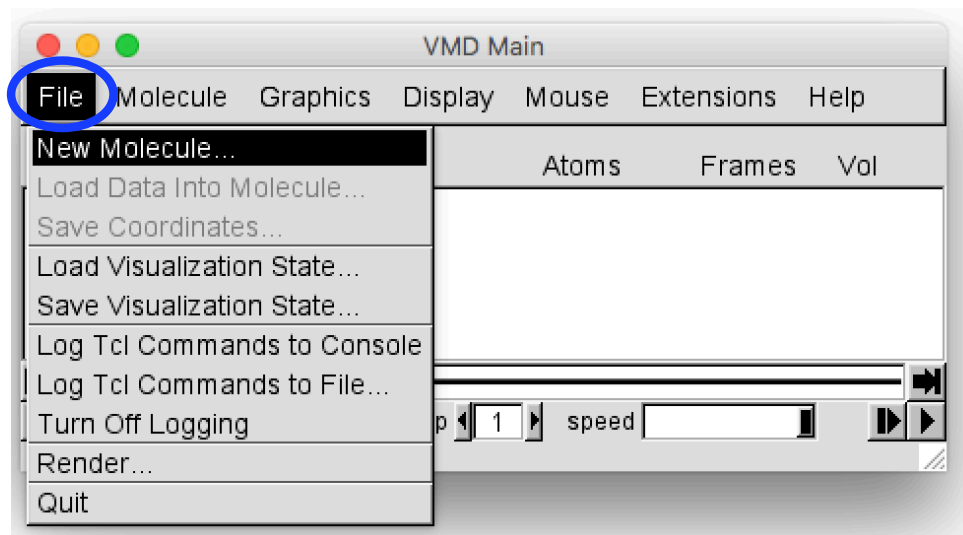


# Hands-on: Visualization – Charge Density

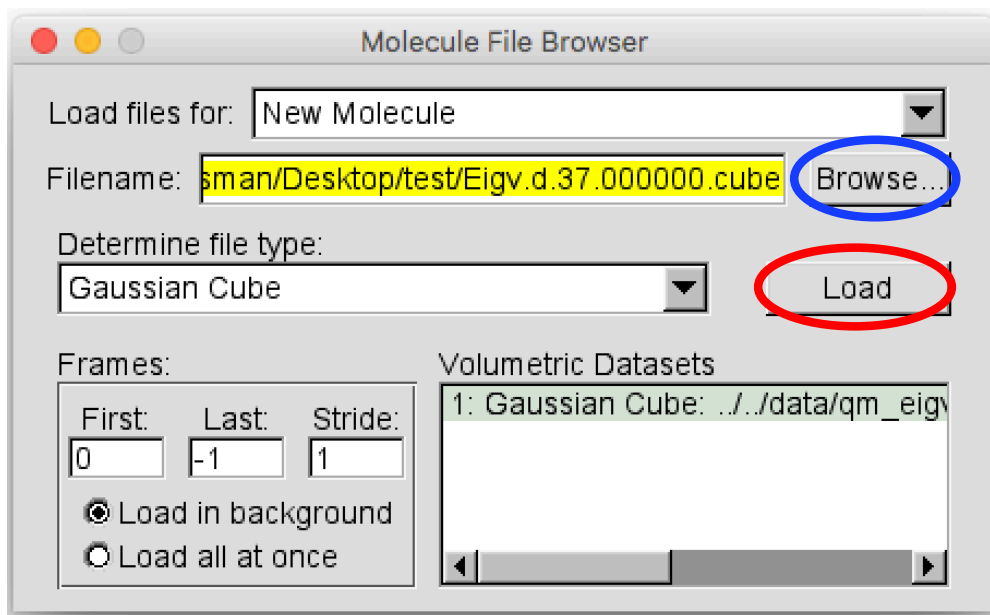
**Load LUMO charge density**  
(Lowest Unoccupied Molecular Orbital)

**Open VMD**

**File -> New Molecule**



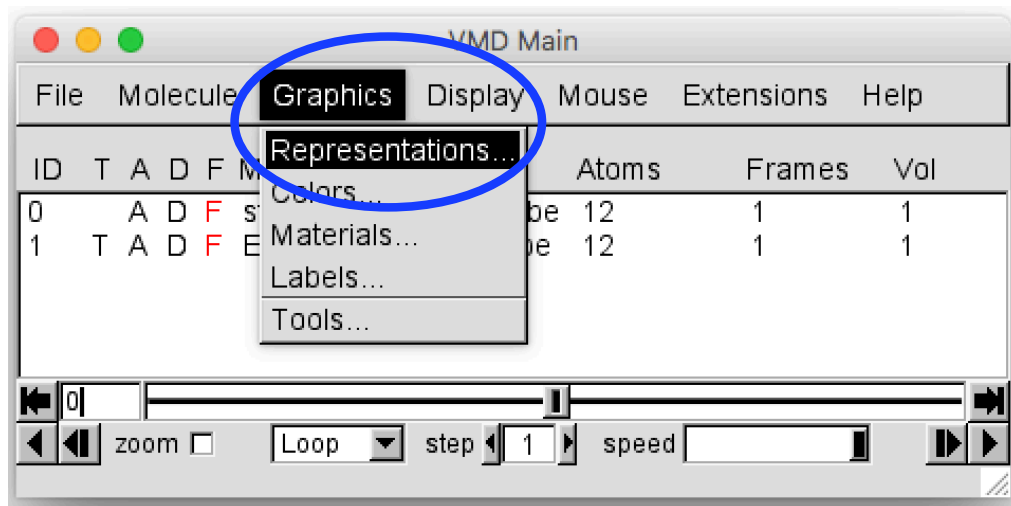
**Browse -> select/path/to/state.37.000000.cube**



**Click Load**

# Hands-on: Visualization - Charge Density

## Graphics -> Representations





# Hands-on: Visualization - Charge Density

## Graphics -> Representations

Graphical Representations

Selected Molecule  
1: Eigv.d.37.000000.cube

Create Rep Delete Rep

Style	Color	Selection
Isosurface	ColorID 1	<volume>

Selected Atoms  
all

Draw style | Selections | Trajectory | Periodic | Material

Coloring Method  
ColorID 1 Opaque

Drawing Method  
Isosurface Default

Range 17191 17313 Vol vol0: Eigv.d.37

Isovalue -0.068398

Step 1 Draw Solid Surface

Size 1 Show Isosurface

Apply Changes Automatically Apply

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

