

Introduction to Non-Adiabatic Quantum Molecular Dynamics

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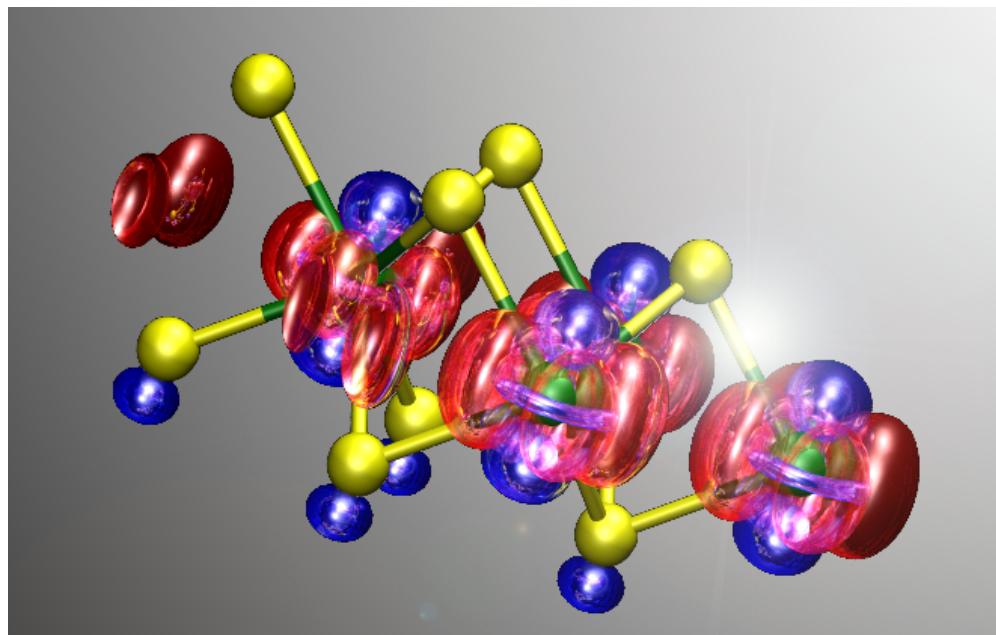
Non-Adiabatic QMD (NAQMD)

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

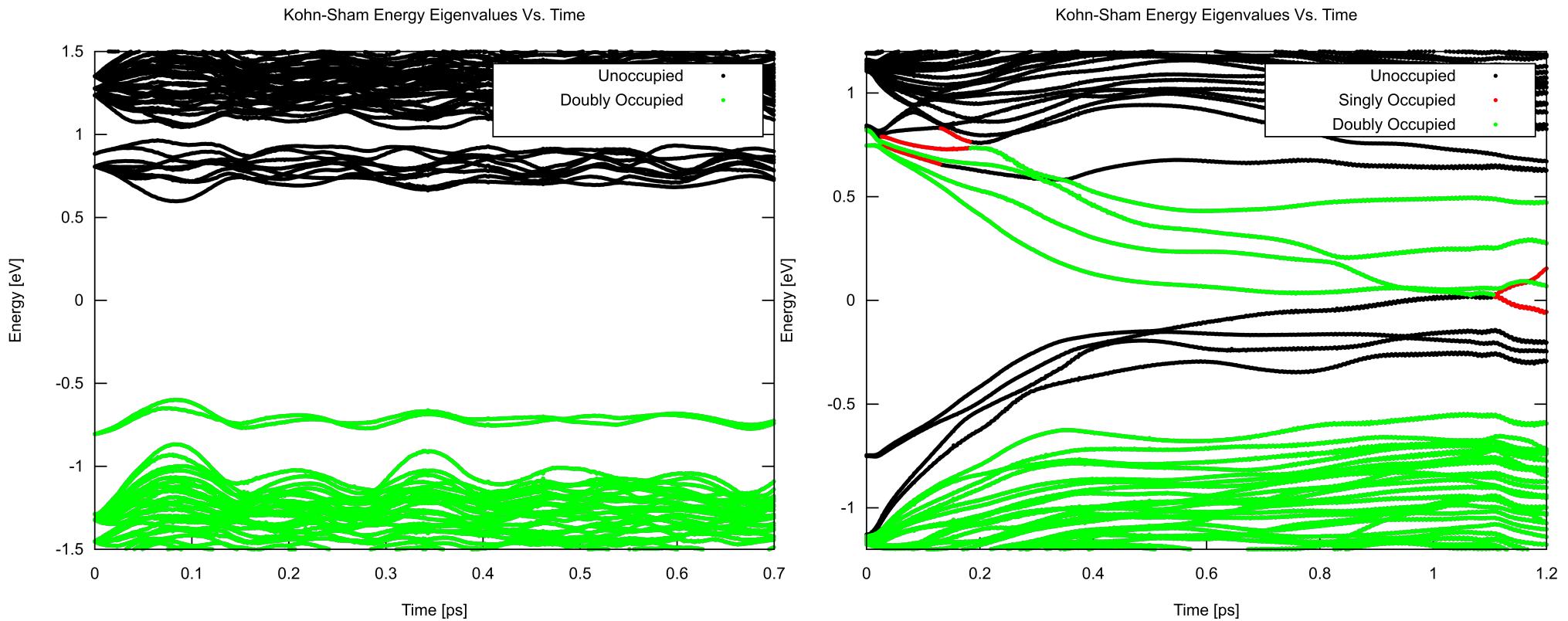
Time-Dependent Density Functional Theory (TDDFT):

- 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 MoSe₂.



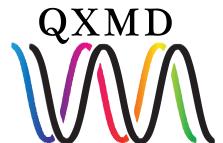
Hands-on: Non-Adiabatic Molecular Dynamics

Overview

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



Materials Genome Innovation
for Computational Software



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          : (dtdddft)
                  :
(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.       : (ltdf_start)
```

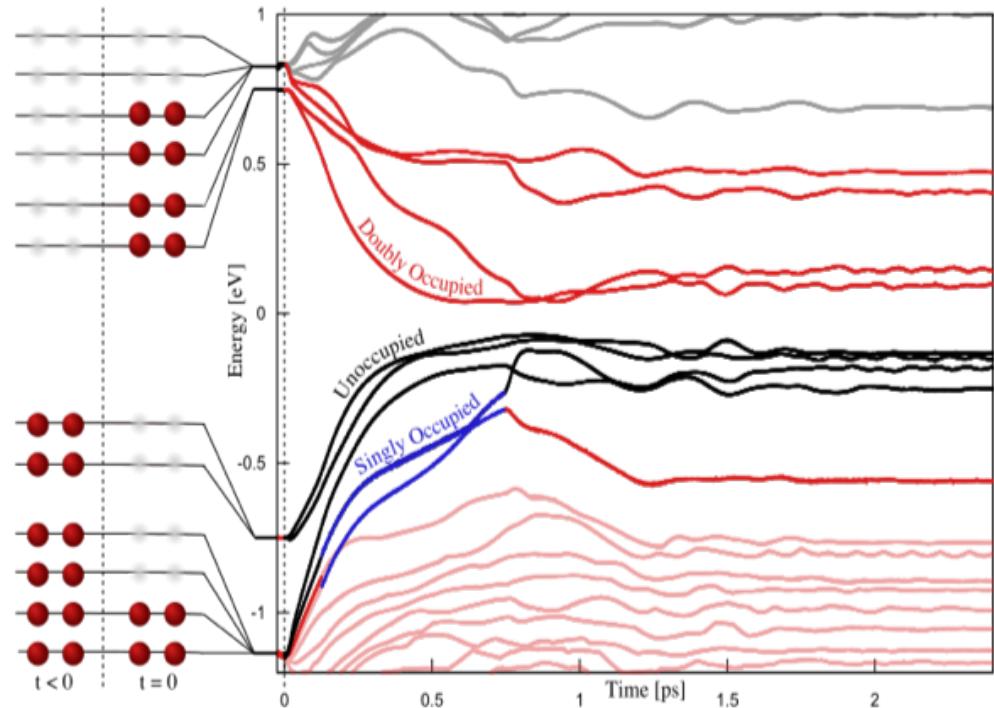
time step: Time step in [a.u.] for numerically integrating TDDFT equations

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: Examine Output Files

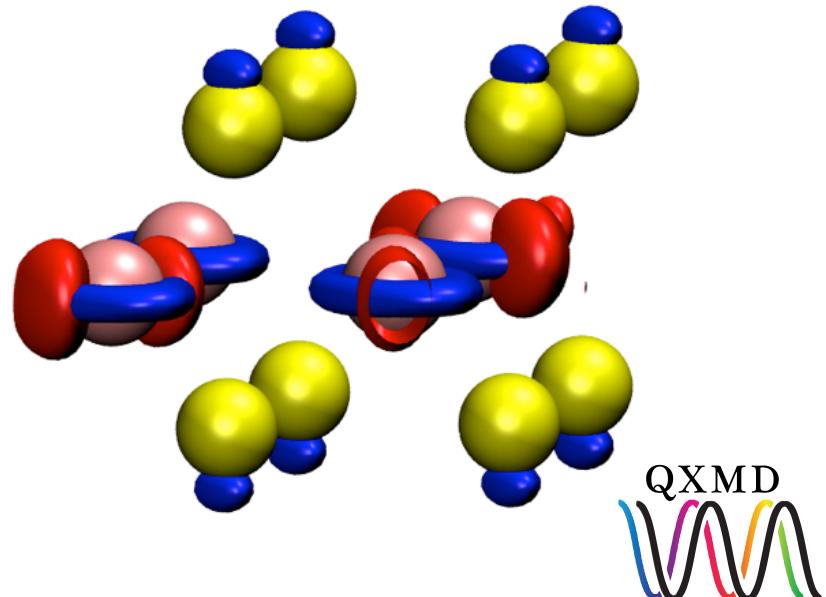
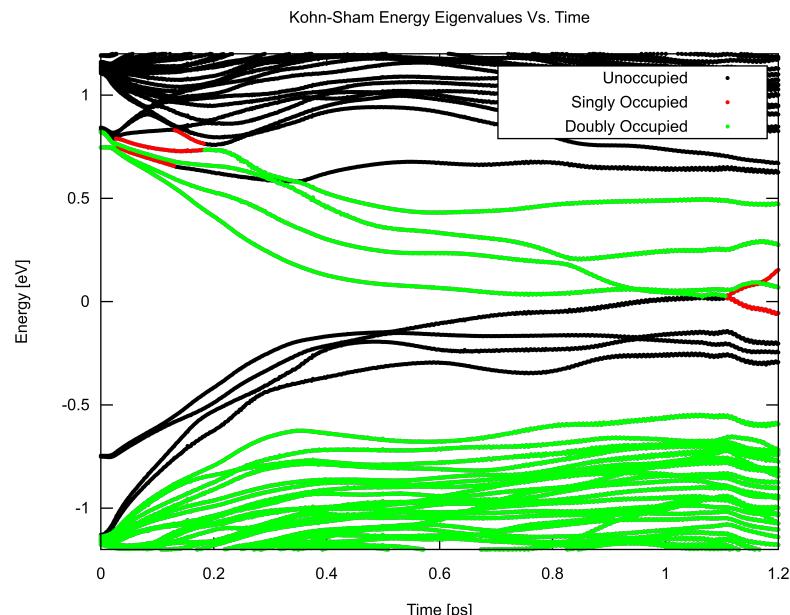
qm_td_eig.d

Eigenvalues of GS & occupations of Excited States		
Time Step	Band Indices	Total # of bands
	0	37
	1	48
	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

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!

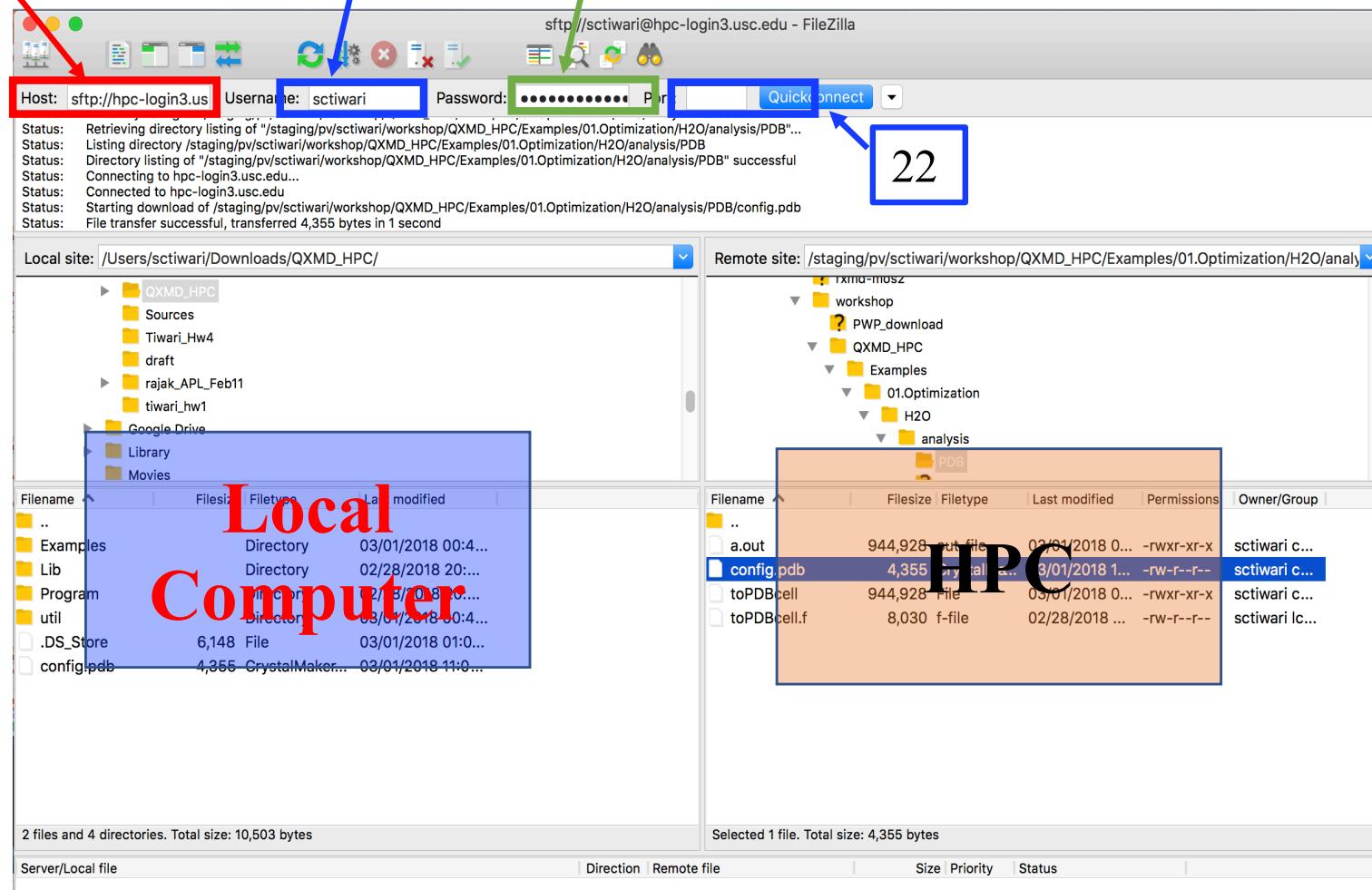
- Use scp or filezilla

Filezilla

hpc-login3.usc.edu

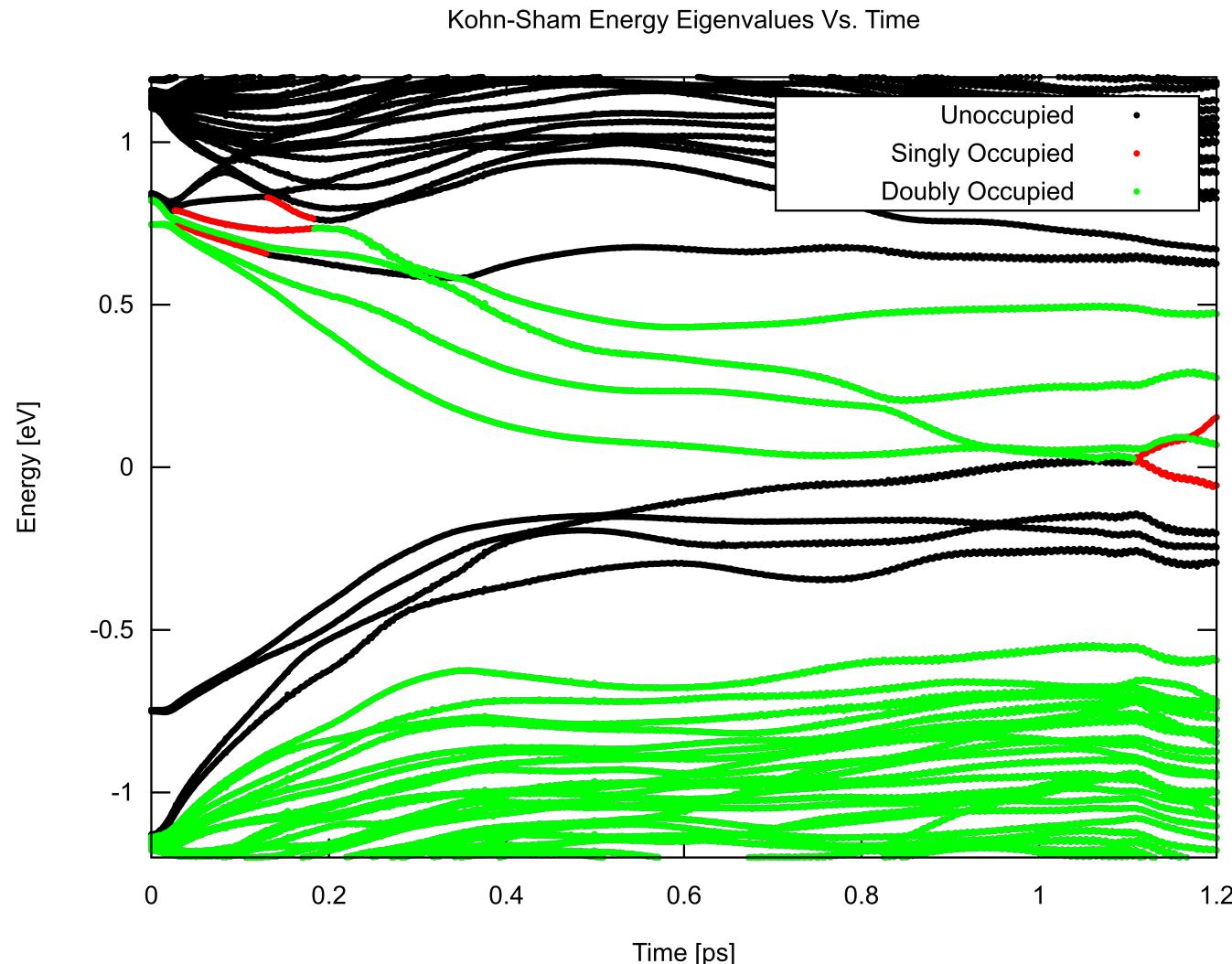
magicsXX

Password



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!

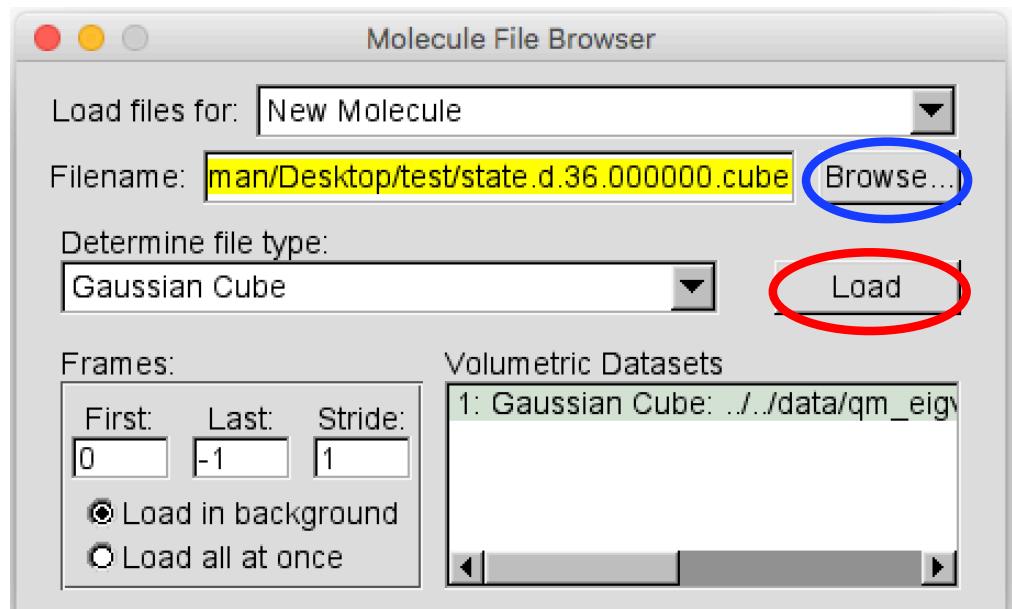
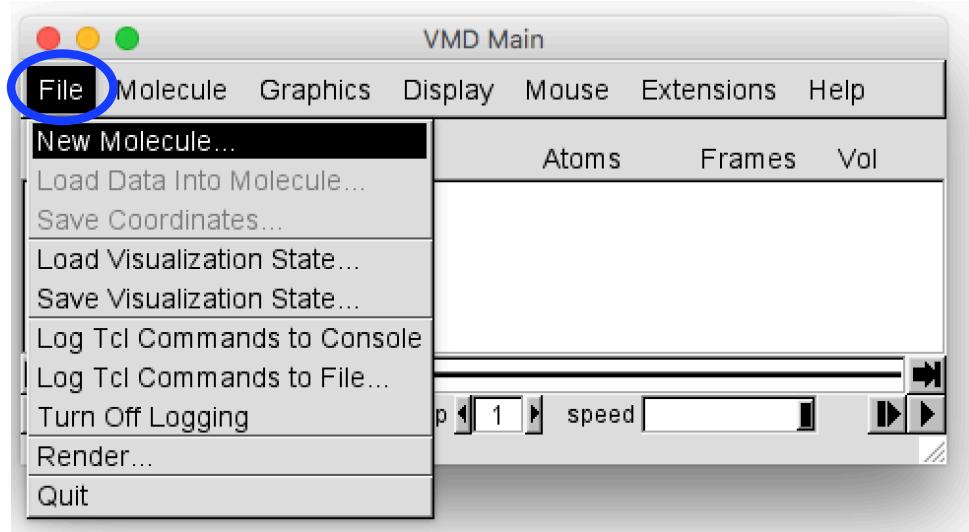
Hands-on: Visualization – Charge Density

Load HOMO charge density
(Highest Occupied Molecular Orbital)

Open VMD
File -> New Molecule

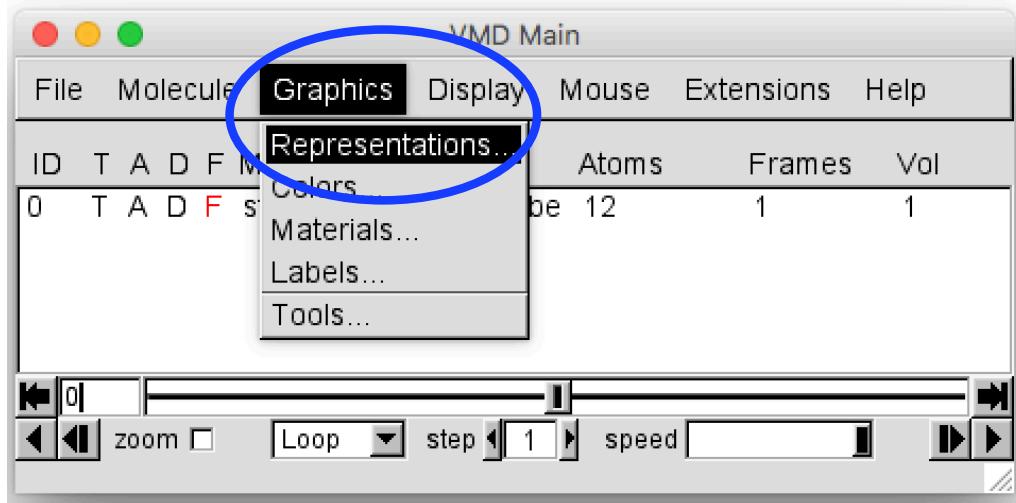
Browse -> select/path/to/state.36.000000.cube

Click Load



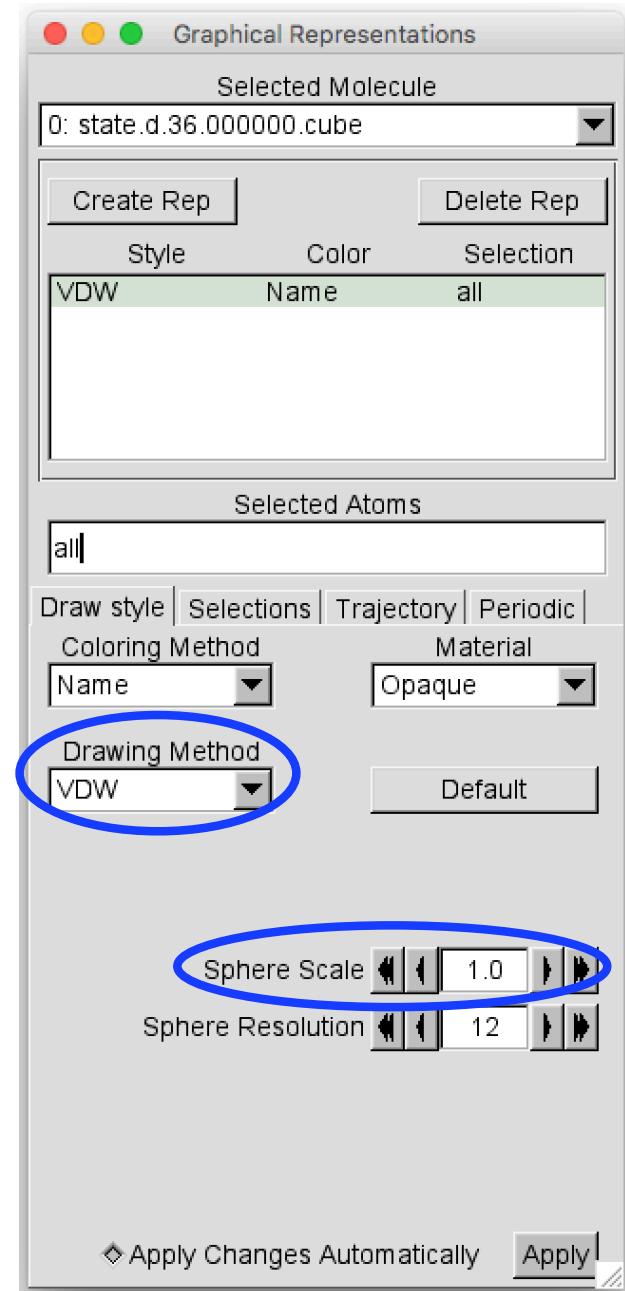
Hands-on: Visualization - Charge Density

Graphics -> Representations



Drawing Method: VDW

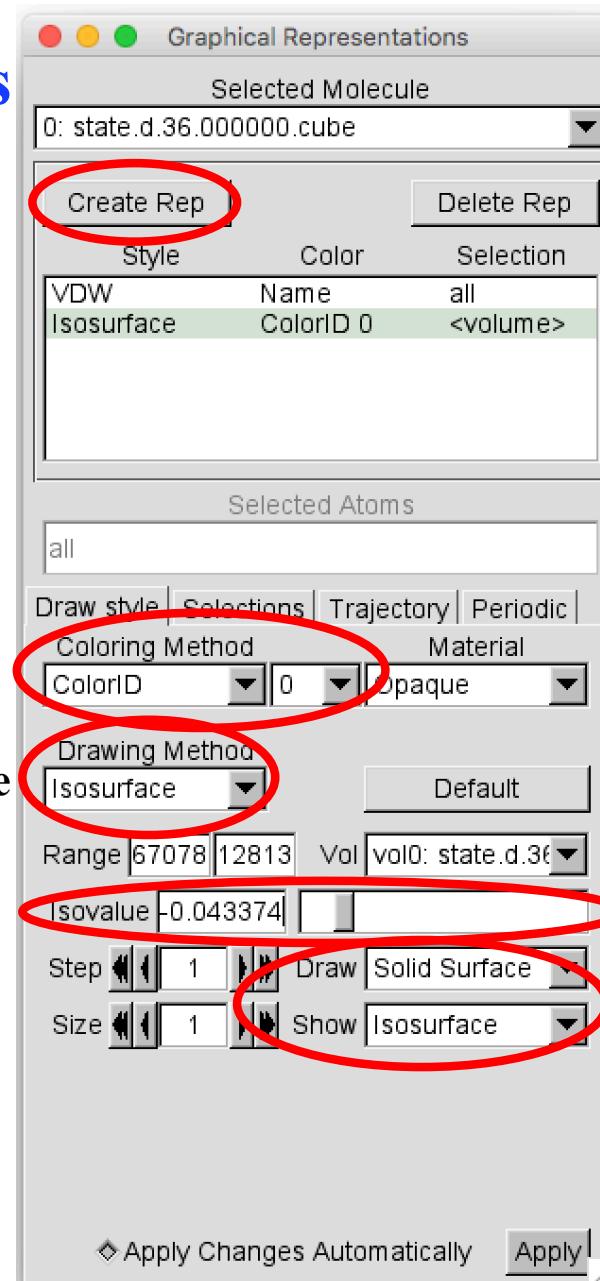
Sphere Scale: 0.3



Hands-on: Visualization - Charge Density

Graphics -> Representations

Click Create Rep



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

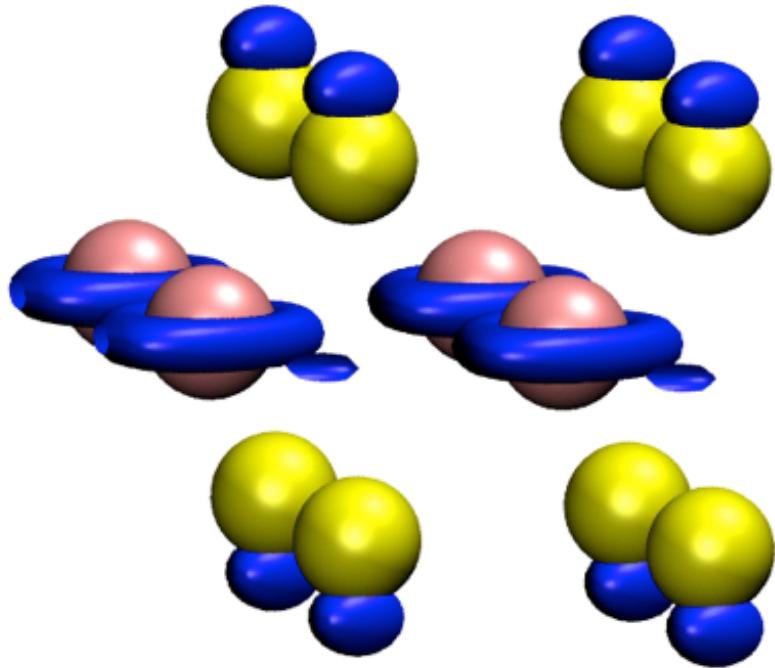
Set **Drawing Method**: Isosurface

Set **Isovalue**: your choice!

Set **Draw**: Solid Surface

Set **Show**: Isosurface

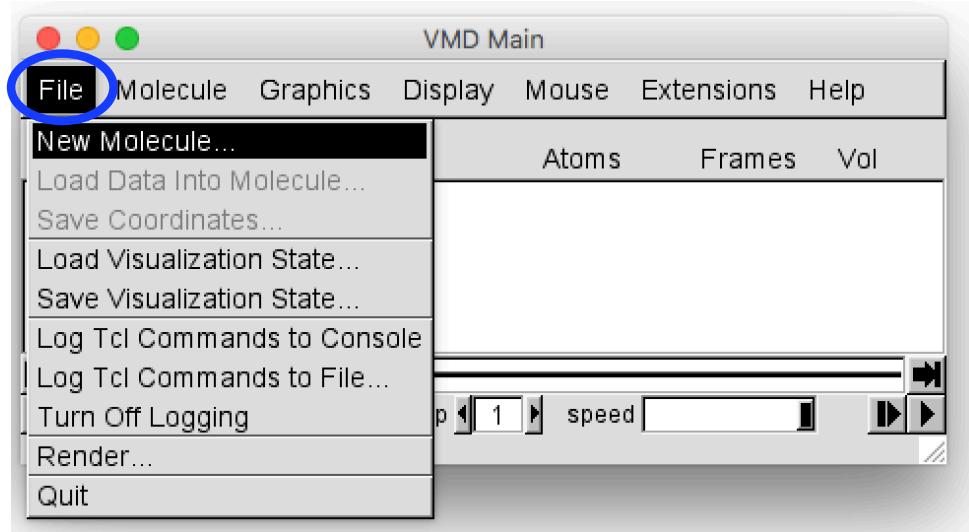
Hands-on: Visualization - Charge Density



Hands-on: Visualization – Charge Density

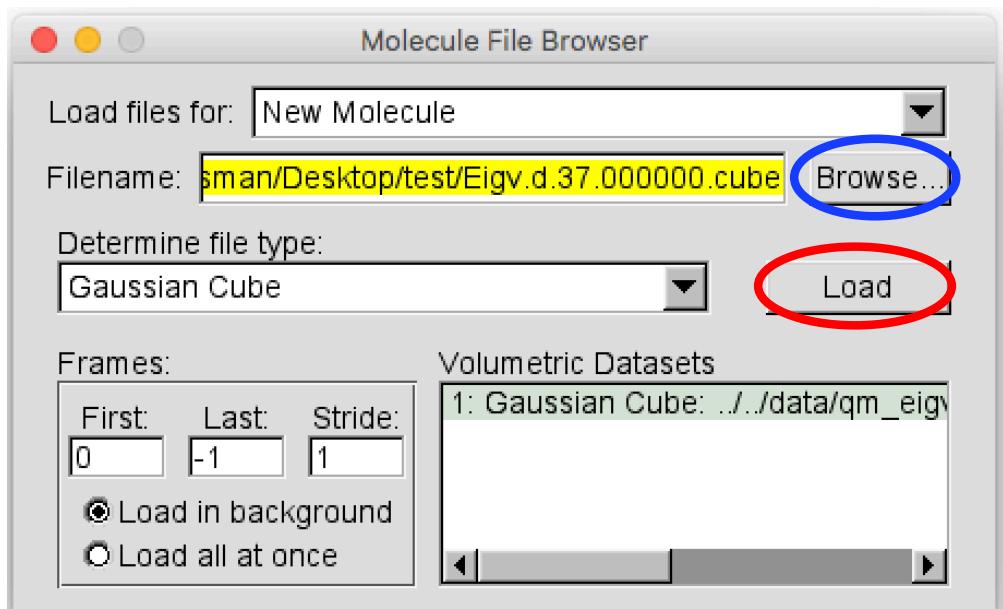
Load LUMO charge density
(Lowest Unoccupied Molecular Orbital)

Open VMD
File -> New Molecule



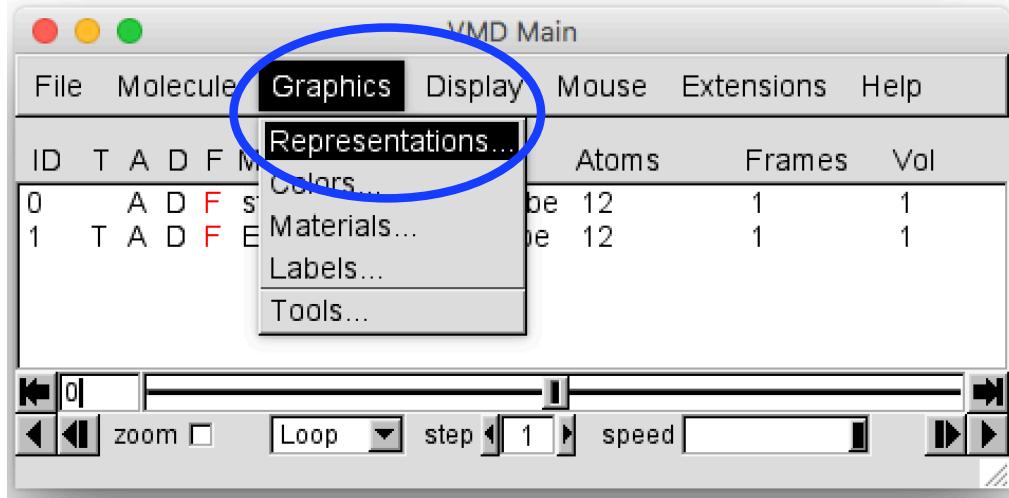
Browse -> select/path/to/state.37.000000(cube)

Click Load



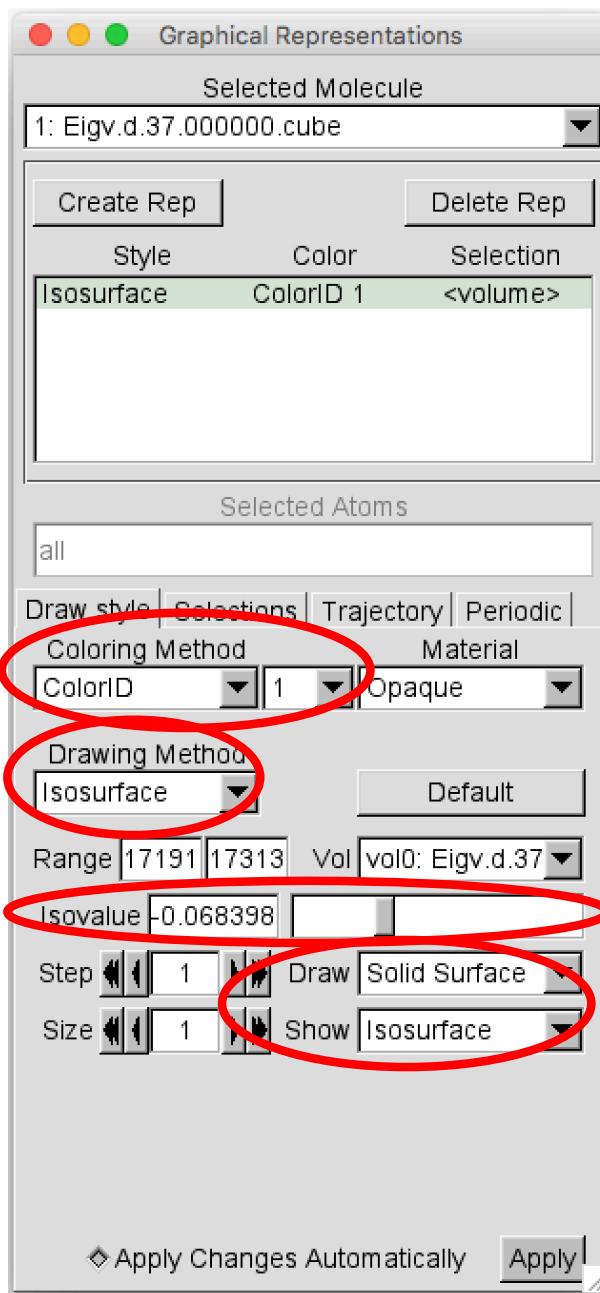
Hands-on: Visualization - Charge Density

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

