Introduction to Non-Adiabatic Quantum Molecular Dynamics

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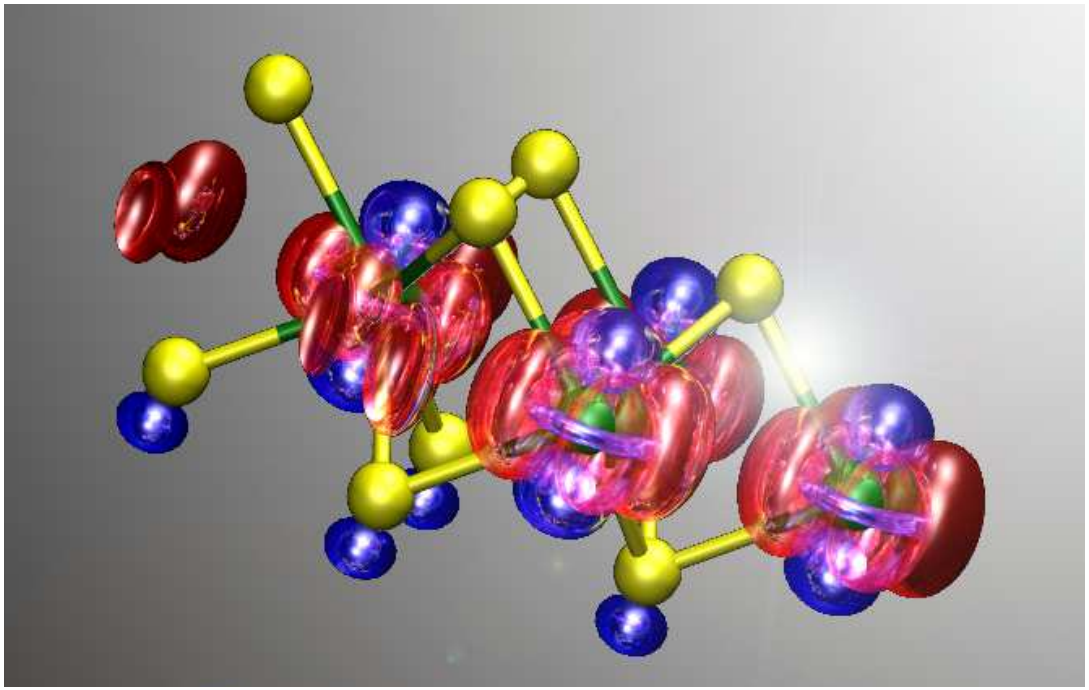
Non-Adiabatic QMD (NAQMD)

Non-Adiabatic QMD (NAQMD):

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

Time-Dependent Density Functional Theory (TDDFT):

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



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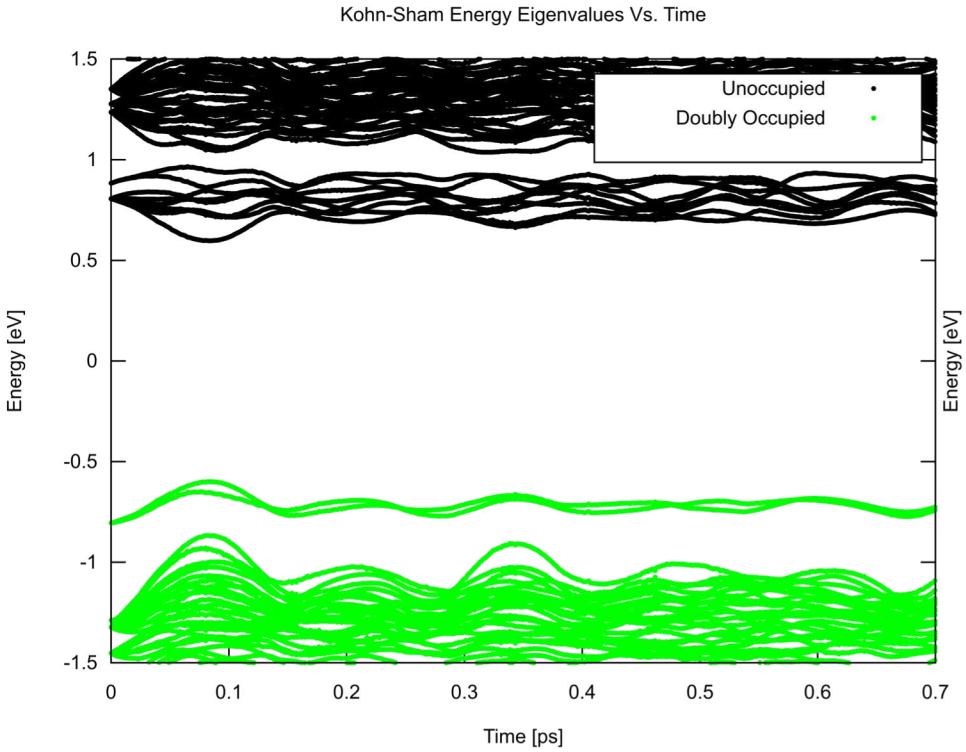
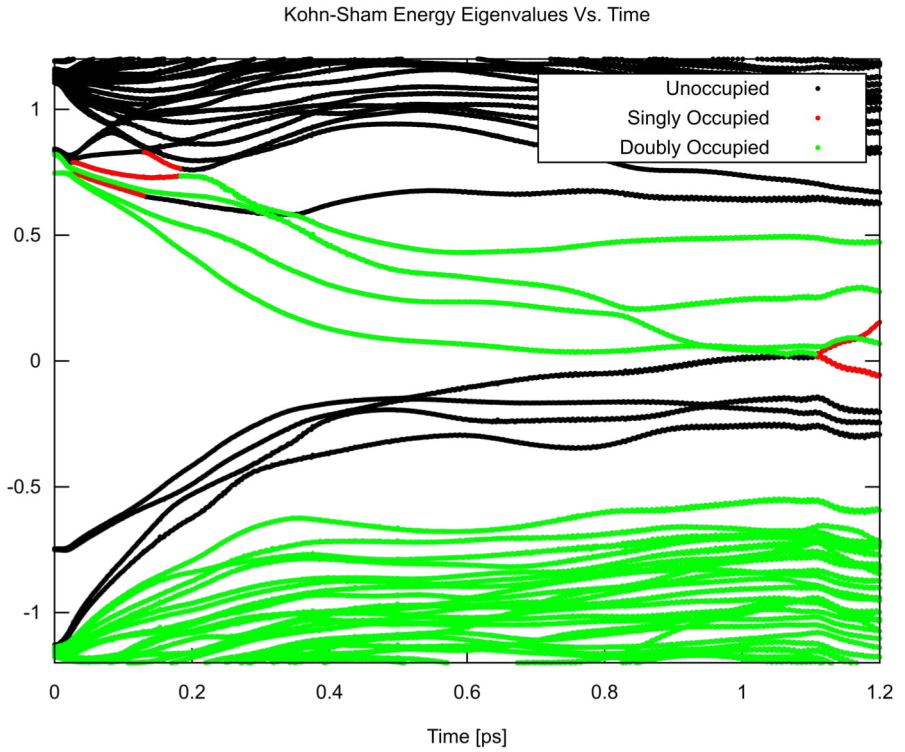
Adiabatic Vs. Non-Adiabatic QMD

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





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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

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Hands-on: Execute NAQMD Simulation

Goal: Perform NAQMD simulation of monolayer $MoSe_2$

1. Log-in to HPC:

```
$ssh magicsXX@hpc-scec.usc.edu
```

2. Navigate to QXMD Example directory:

```
$ cd staging/QXMD_Session/QXMD/Example/
```

3. Change to 05_NAQMD/01_MoSe2 directory

```
$ cd 05_NAQMD/01_MoSe2
$ls
analysis      control      data      job.slurm
```

4. Submit NAQMD job

```
$ sbatch job.slurm
```

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Hands-on: Examine Input File

```
*TDDFT-MD
(on/off)                :
   .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
```

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Hands-on: Examine Input File

```
*TDDFT-MD
(on/off)          :
   .true.         : (ltddft)
                  :
(FSSH-switch)     :
   .true.         : (lfssh_switch)
```

on/off: **True**: Run QMD based on TDDFT[1]
False: Run QMD based on DFT

FSSH-switch: **True**: Allow electrons to hop between bands[2]
False: Electron occupations held fixed

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[1]Gross, E. K. U., and W. Kohn. *Adv. Quantum Chem.* **21**, 255-291, (1990)
[2]Tully, John C. *J. Chem. Phys.* **93.2**, 1061-1071 (1990)

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Hands-on: Examine Input File

```
*TDDFT-MD
(time step)          :
    0.04d0           : (dttddft)
                     :
(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

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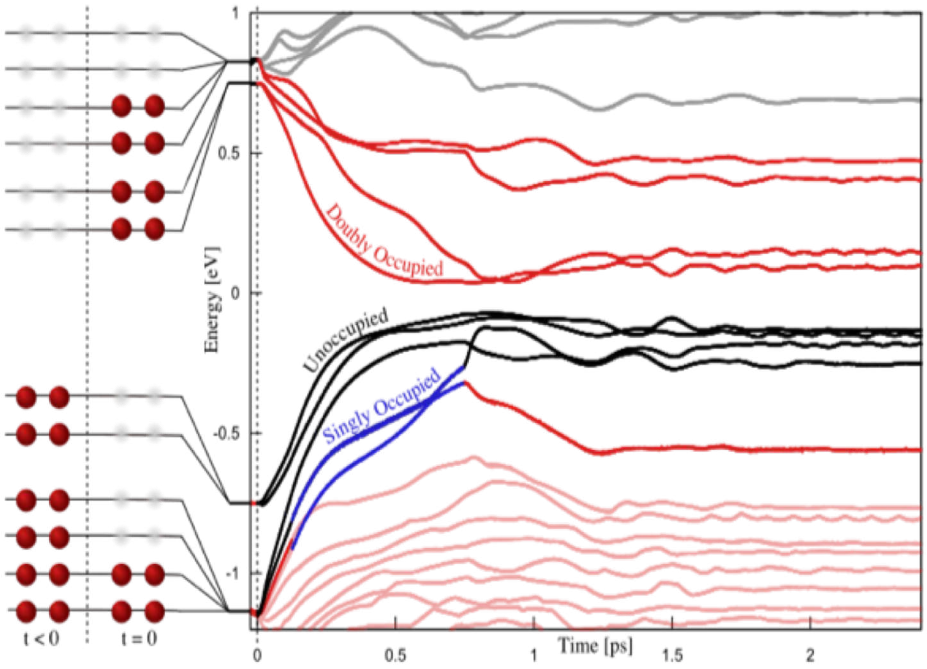
Hands-on: Examine Input File

```
*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)

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Hands-on: Examine Input File

```
*dump wavefunctions          :
(on/off)                     :
  .true.                     : (ldpwav)
(bands)                      :
   36, 37                    : (ibstt1,ibstt2)
(skip step)                  :
   101                       : (nskip_dpwav)
*end
```

(on/off) – 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

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Hands-on: Examine Output Files

1. Check your current directory:

$ pwd

…staging/QXMD_Session/QXMD/Example/05_NAQMD/01_MoSe2

2. Change to data/ directory

$ cd data

$ls

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*

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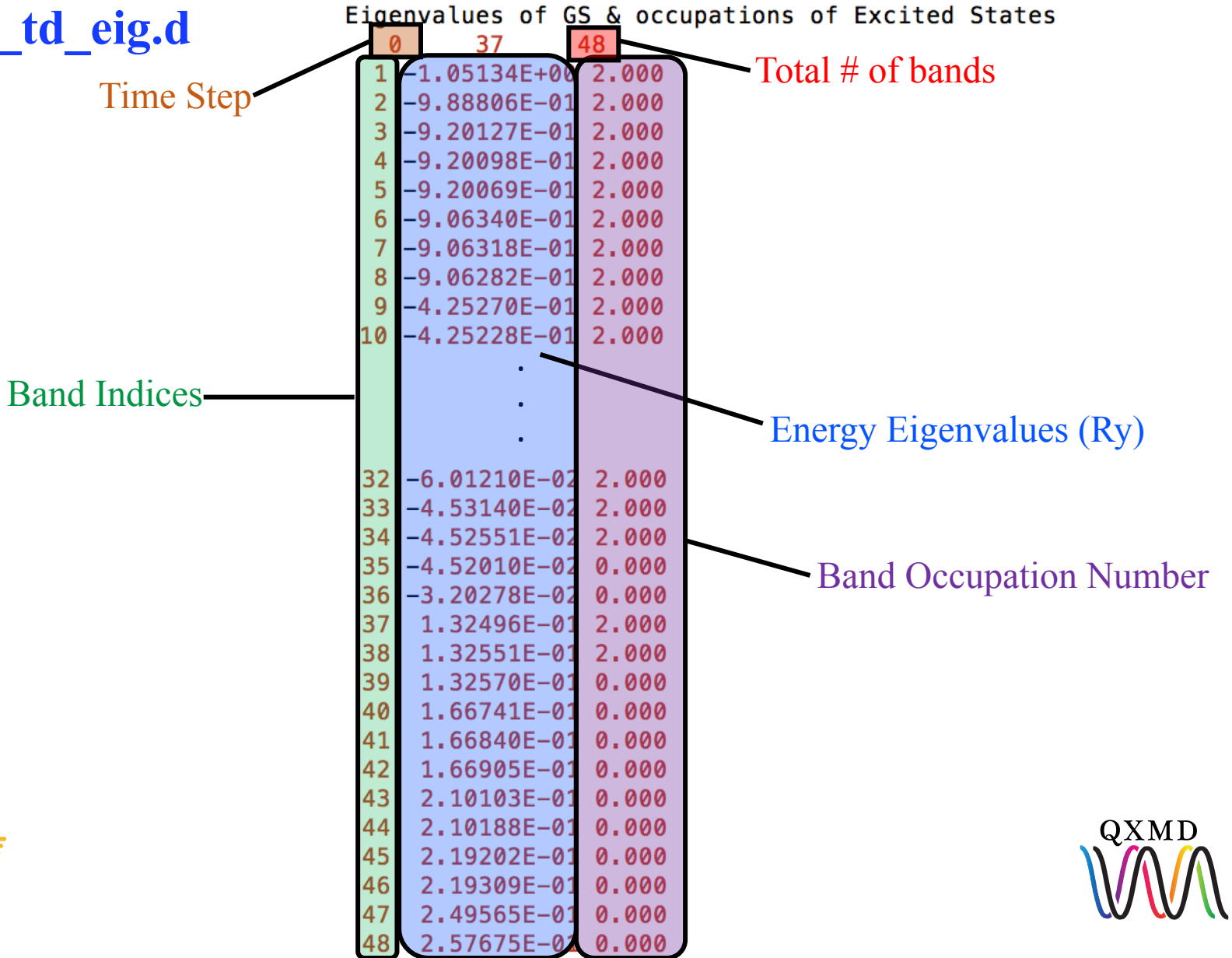
Hands-on: Examine Output Files

$ less qm_td_eig.d



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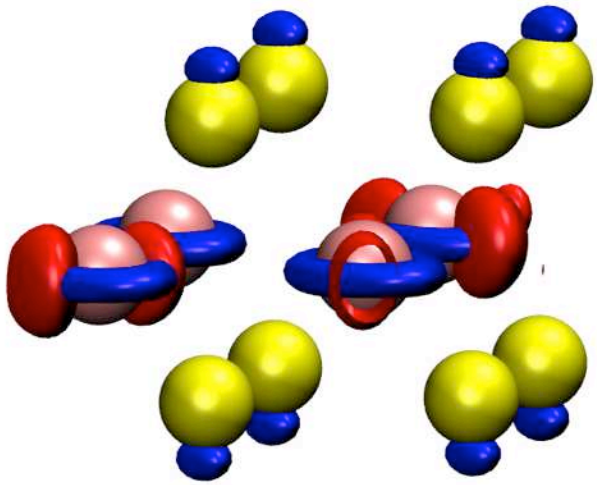
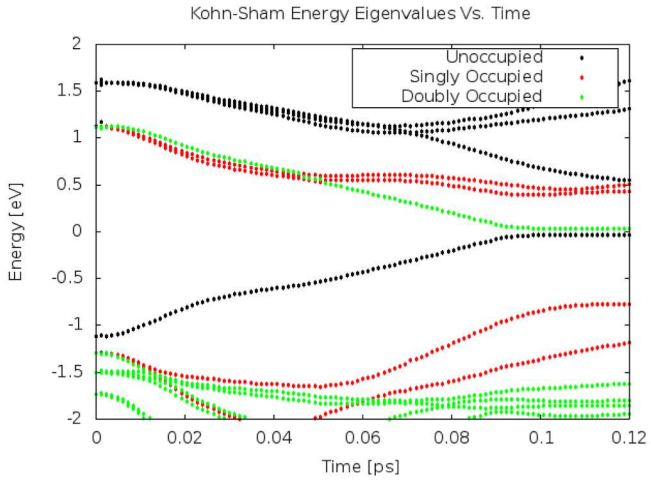
Hands-on: Post-Process Data + Visualization

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



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

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



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Hands-on: Post-Process Data – Charge Density

1. Check your current directory:

```
$ pwd
…staging/QXMD_Session/QXMD/Example/05_NAQMD/01_MoSe2/data
```

2. Change to analysis/GCube directory

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

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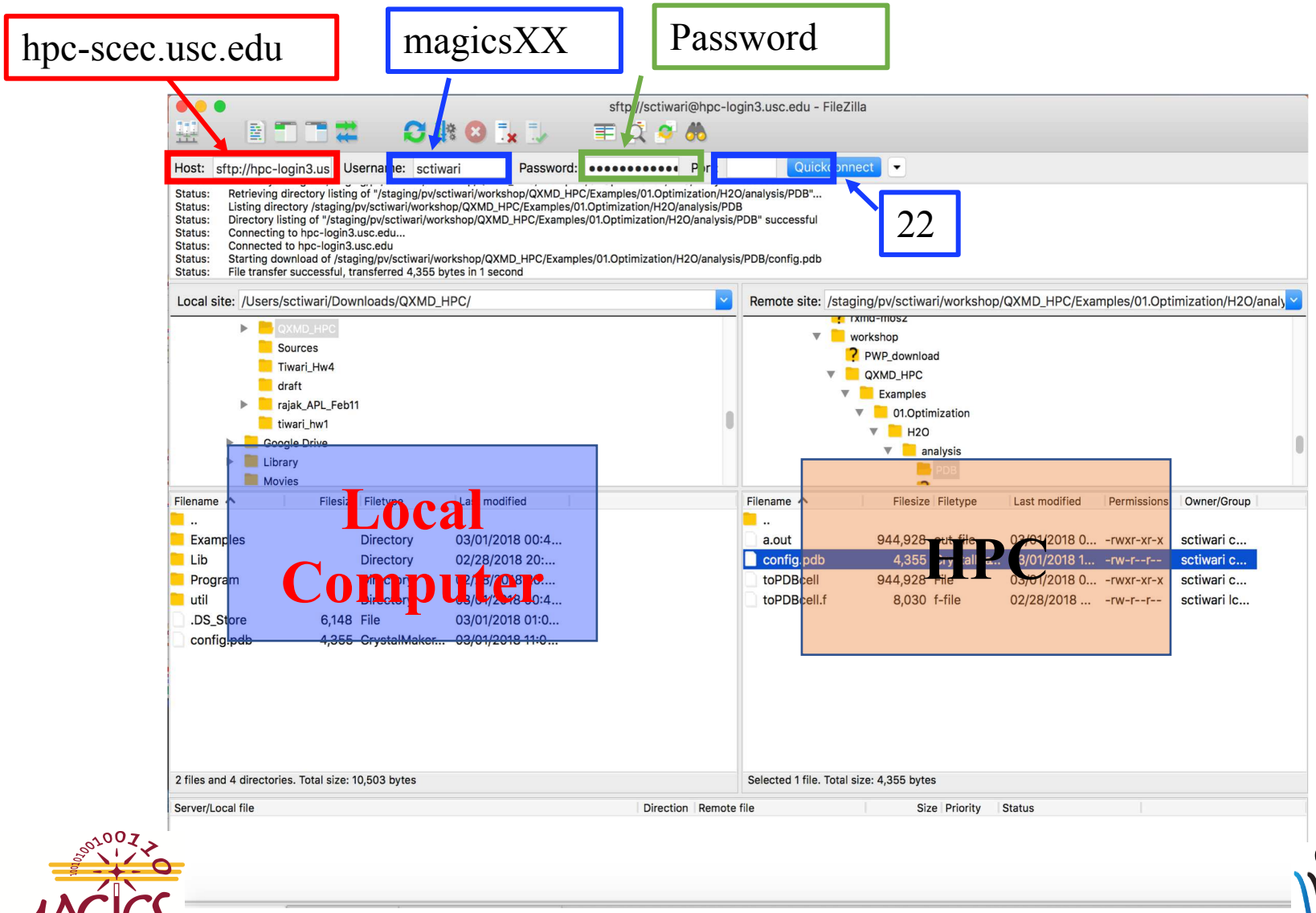
Filezilla



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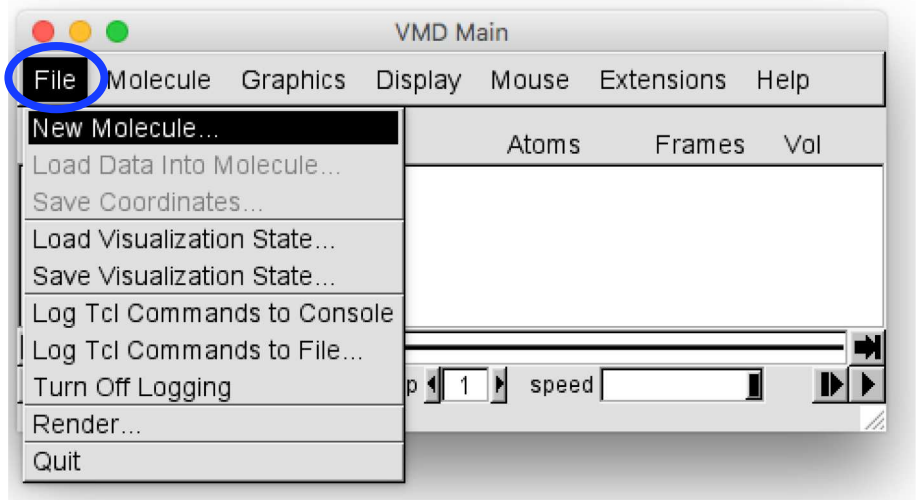
Hands-on: Visualization – Charge Density

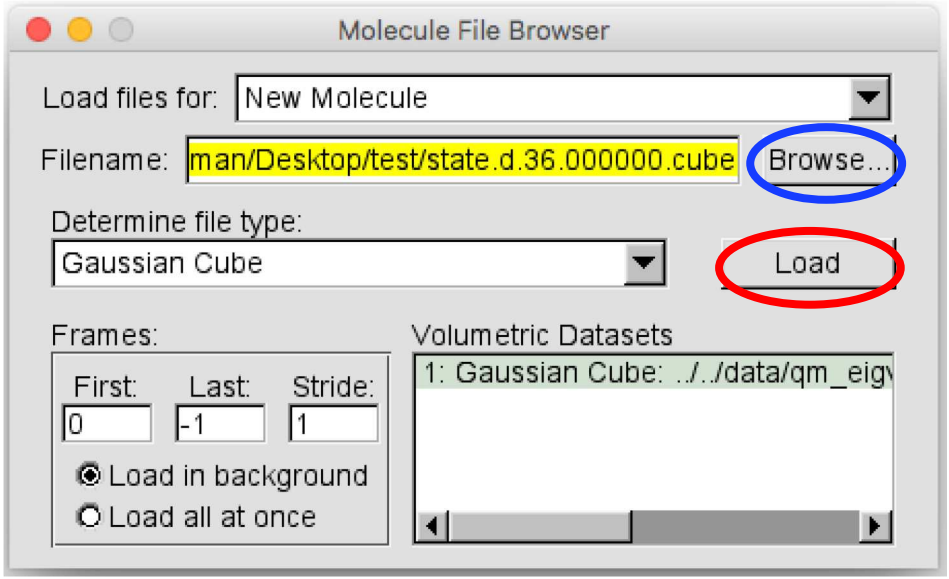
Load HOMO charge density
(Highest Occupied Molecular Orbital)

Open VMD
File -> New Molecule



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

Click Load



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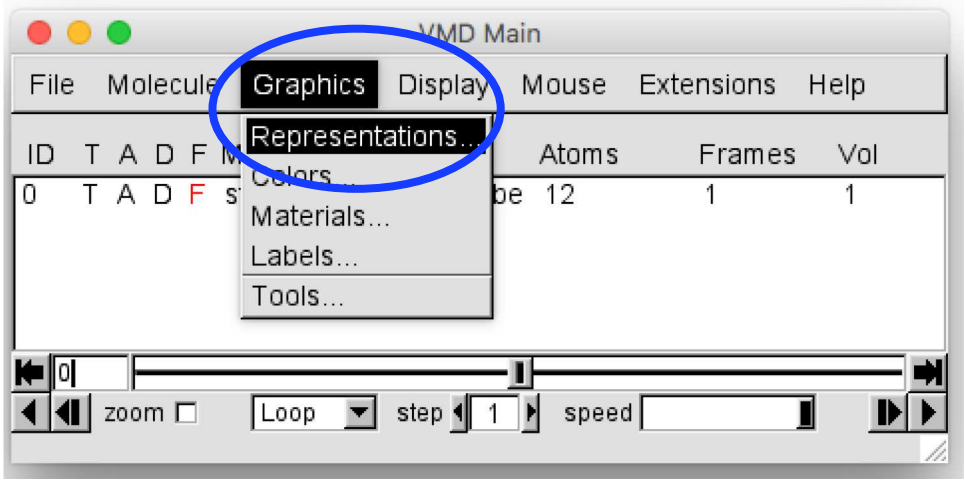
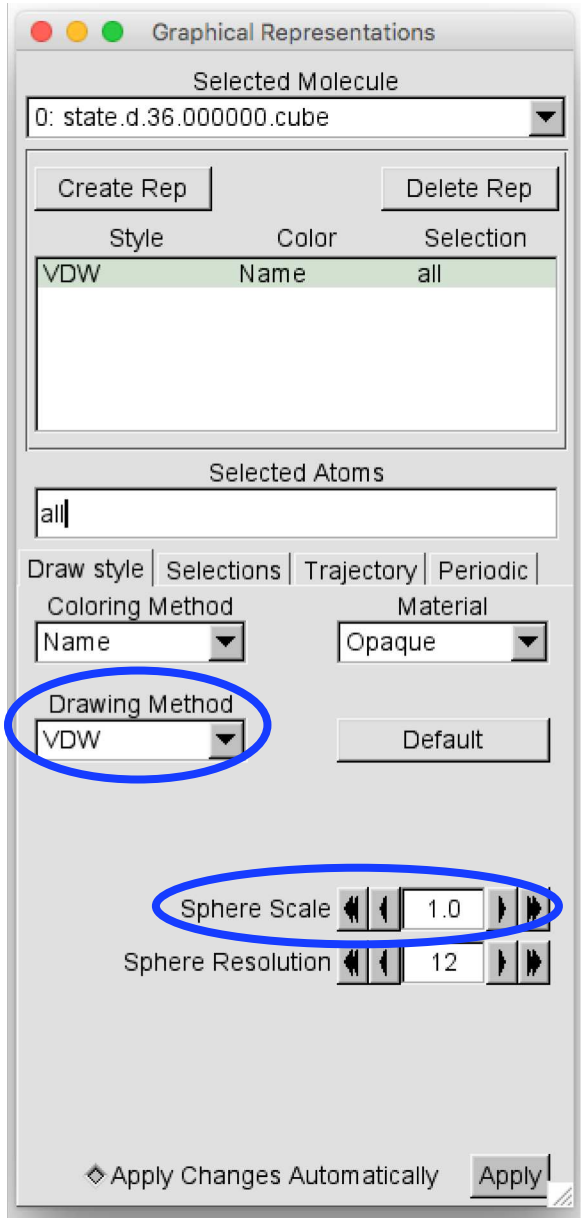
Hands-on: Visualization - Charge Density

Graphics -> Representations





Drawing Method: VDW

Sphere Scale: 0.3

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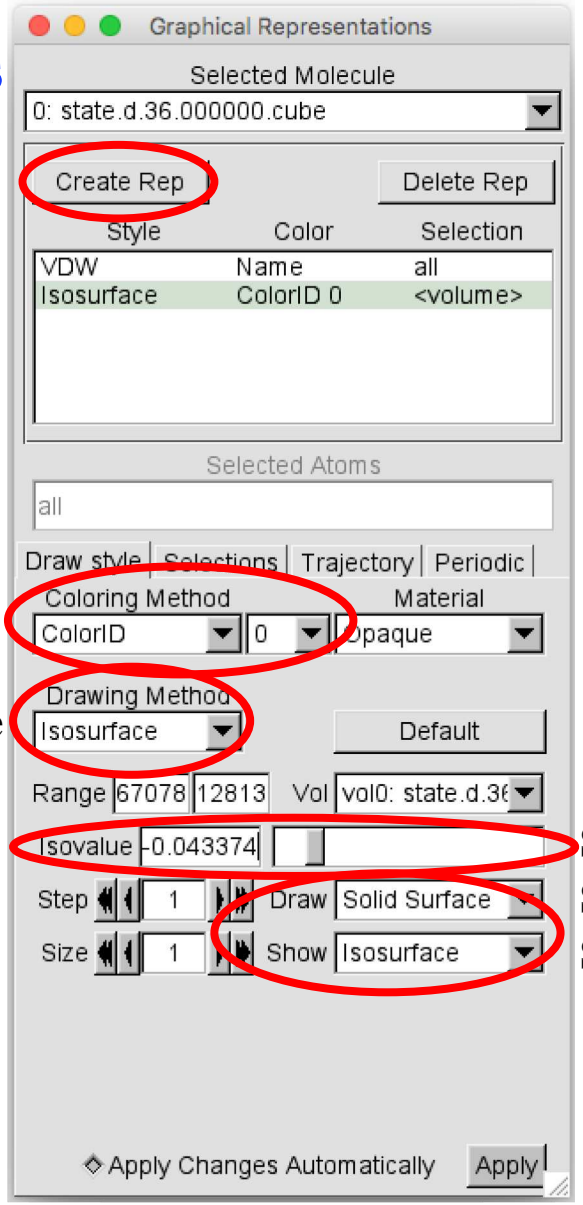
Hands-on: Visualization - Charge Density

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

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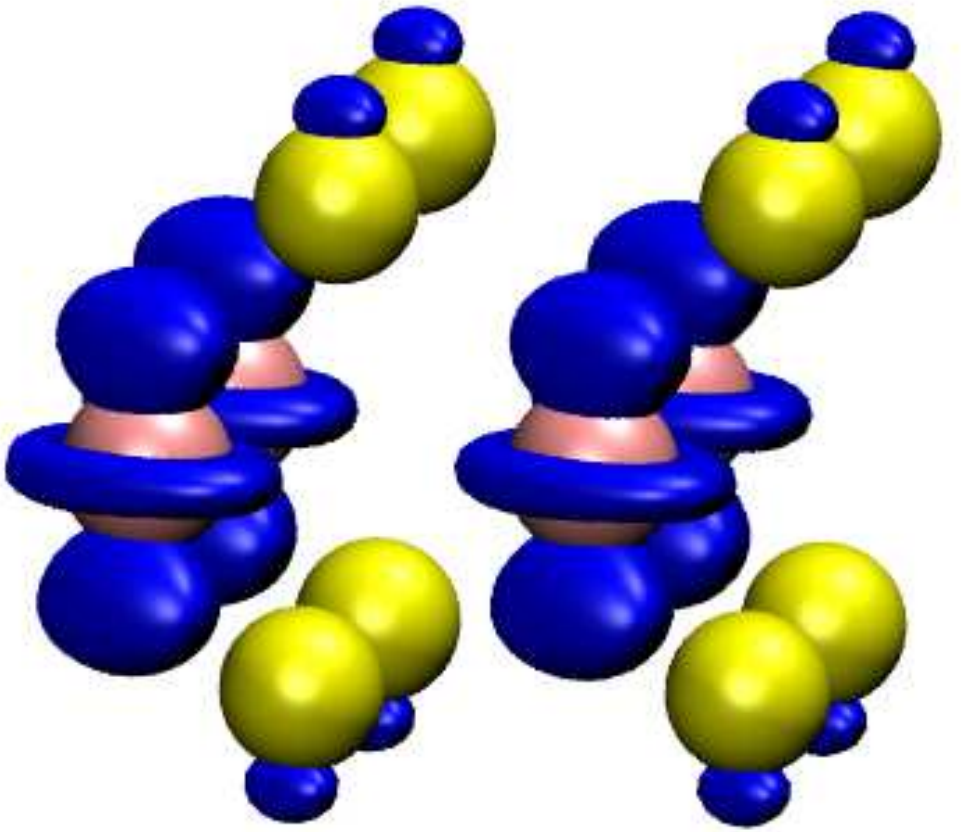
Hands-on: Visualization - Charge Density



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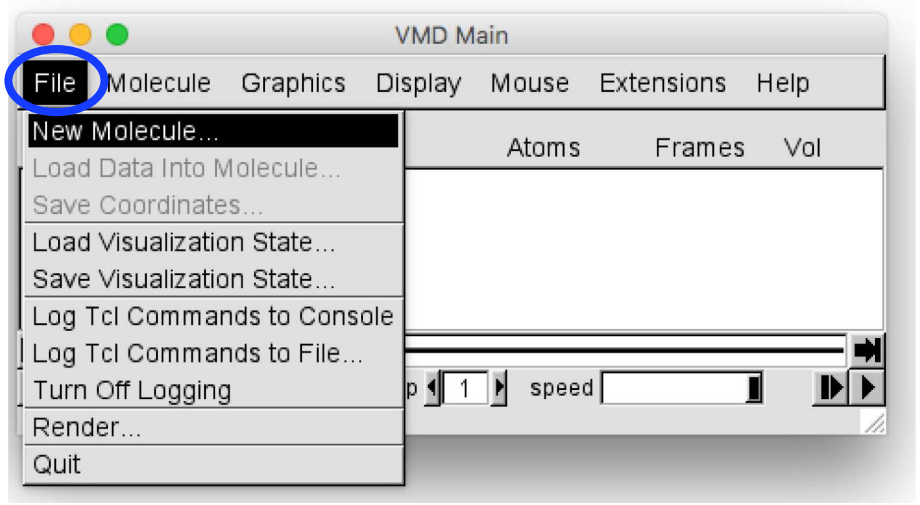
Hands-on: Visualization – Charge Density

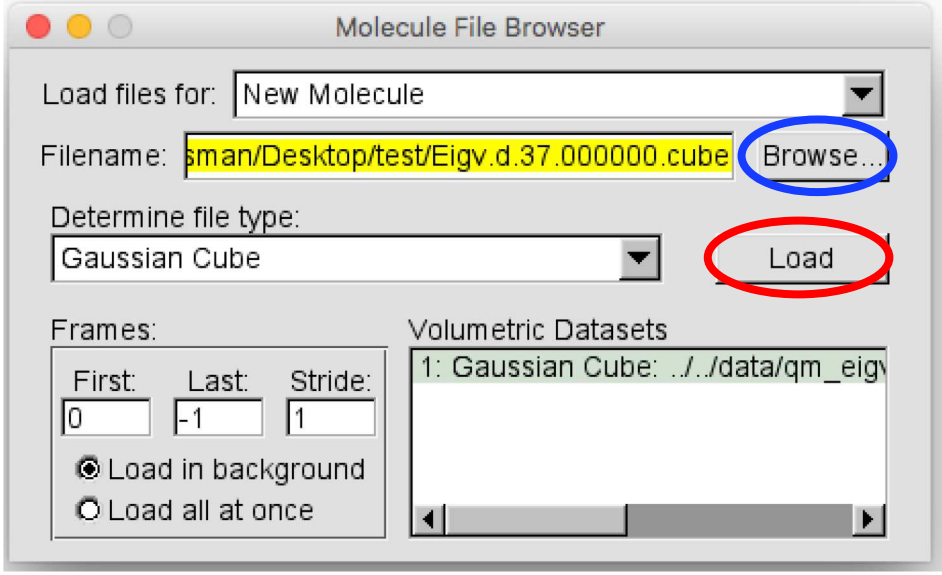
Load LUMO charge density
(Lowest Unoccupied Molecular Orbital)

Open VMD
File -> New Molecule



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

Click Load



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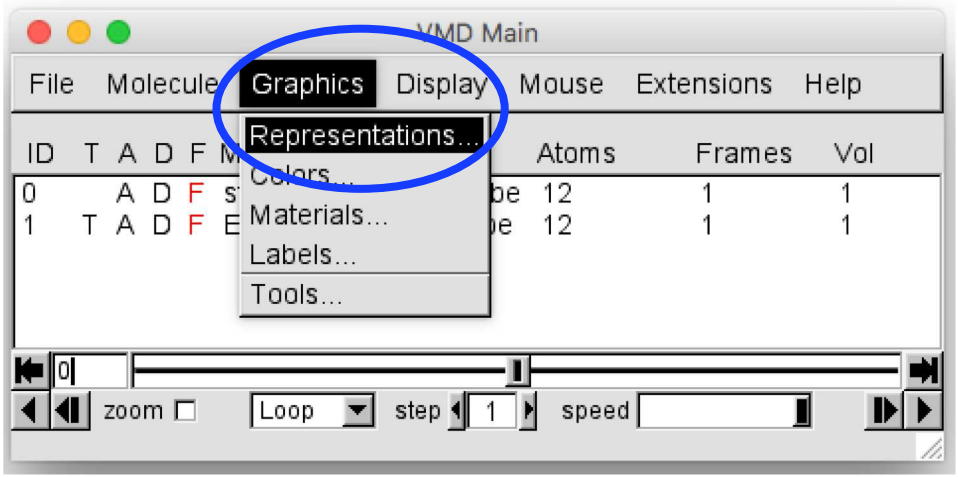
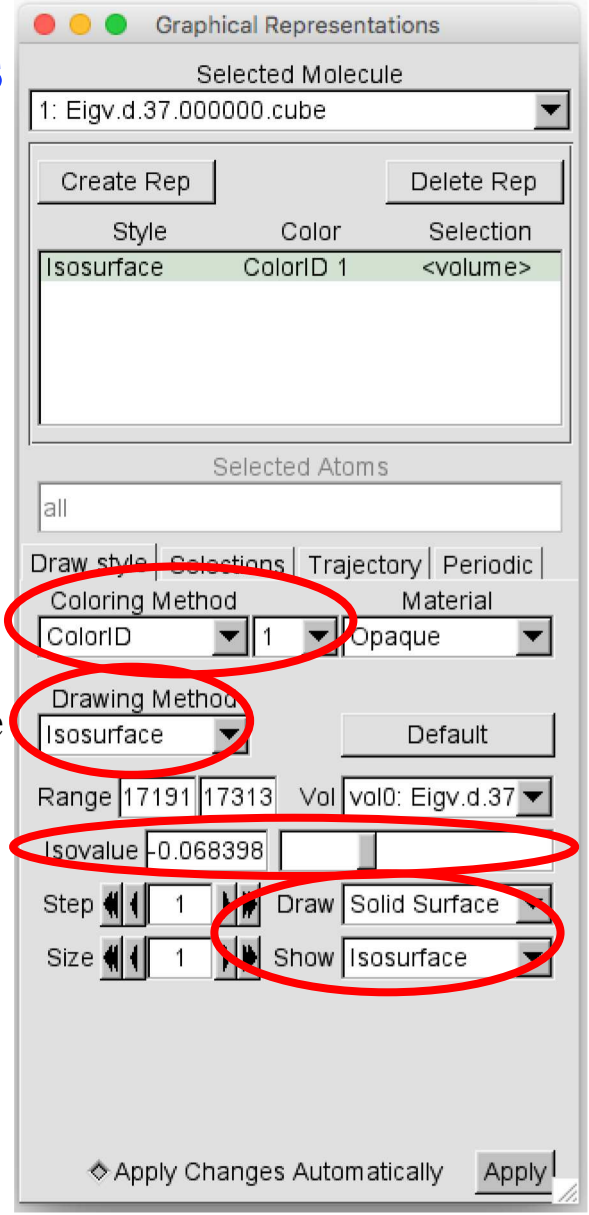
Hands-on: Visualization - Charge Density

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

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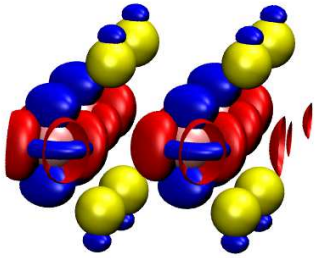
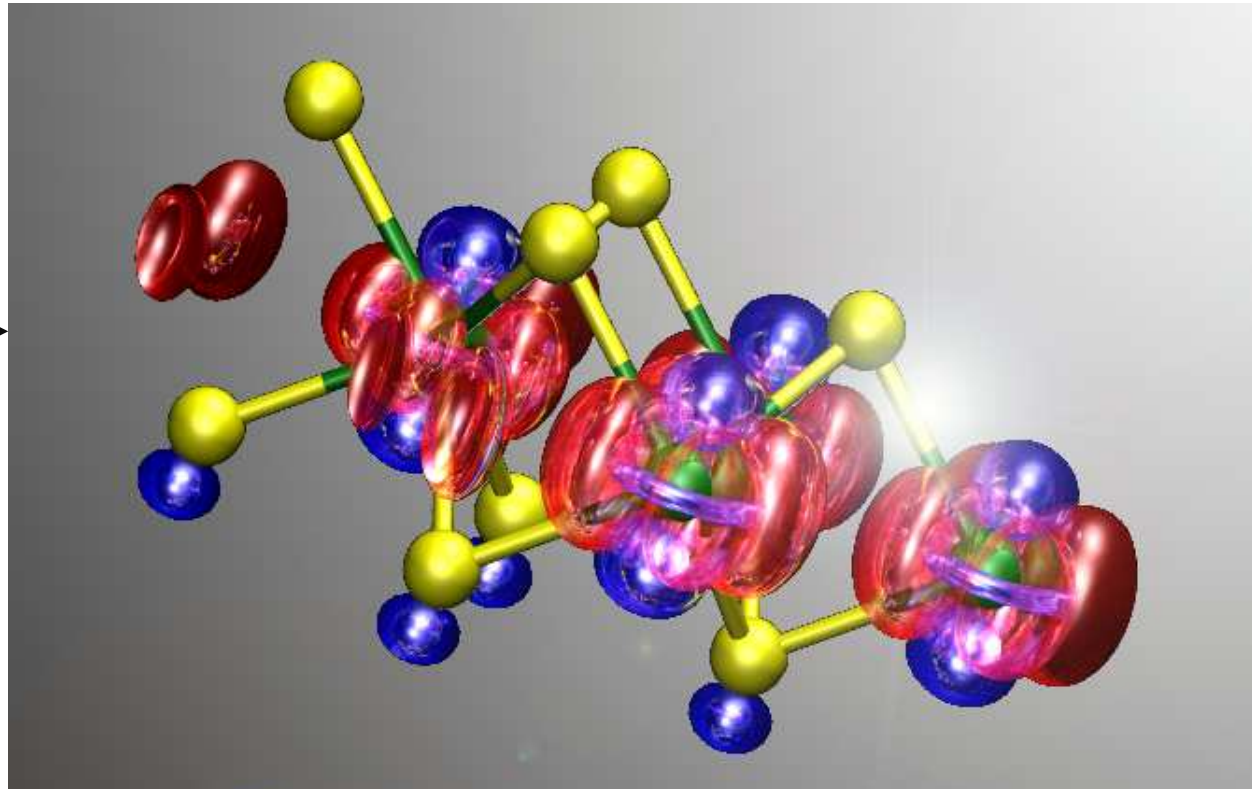
Hands-on: Visualization - Charge Density



POV-Ray



Hands-on: Post-Process Data - Eigenenergies

1. Check your current directory:

```
$ pwd
…staging/QXMD_Session/QXMD/Example/05_NAQMD/01_MoSe2/analysis/GCube
```

2. Change to eig/ directory

```
$ cd ../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

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Hands-on: Visualize Data - Eigenenergies

1. Check your current directory:

```
$ pwd
…staging/QXMD_Session/QXMD/Example/05_NAQMD/01_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!

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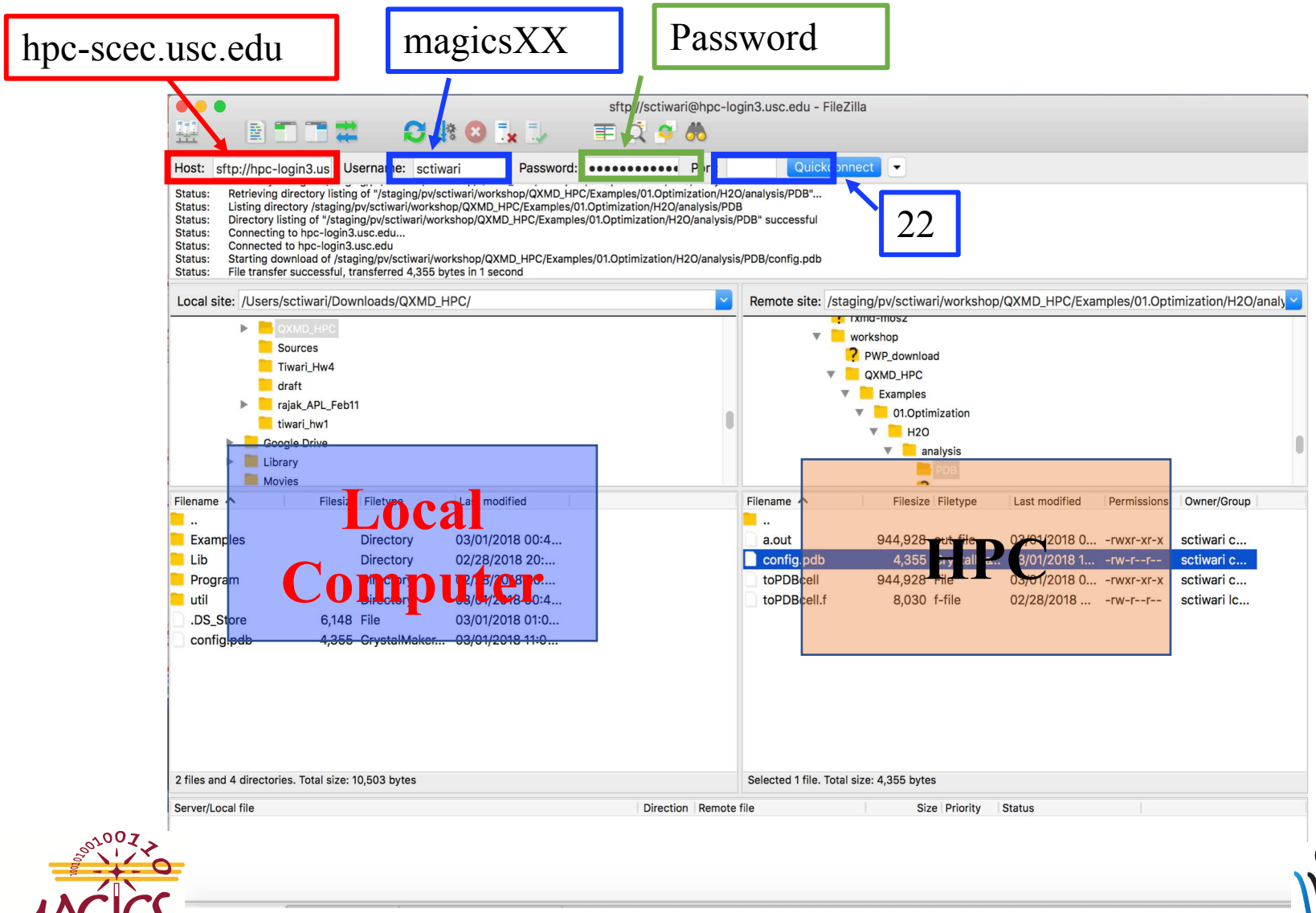
Filezilla



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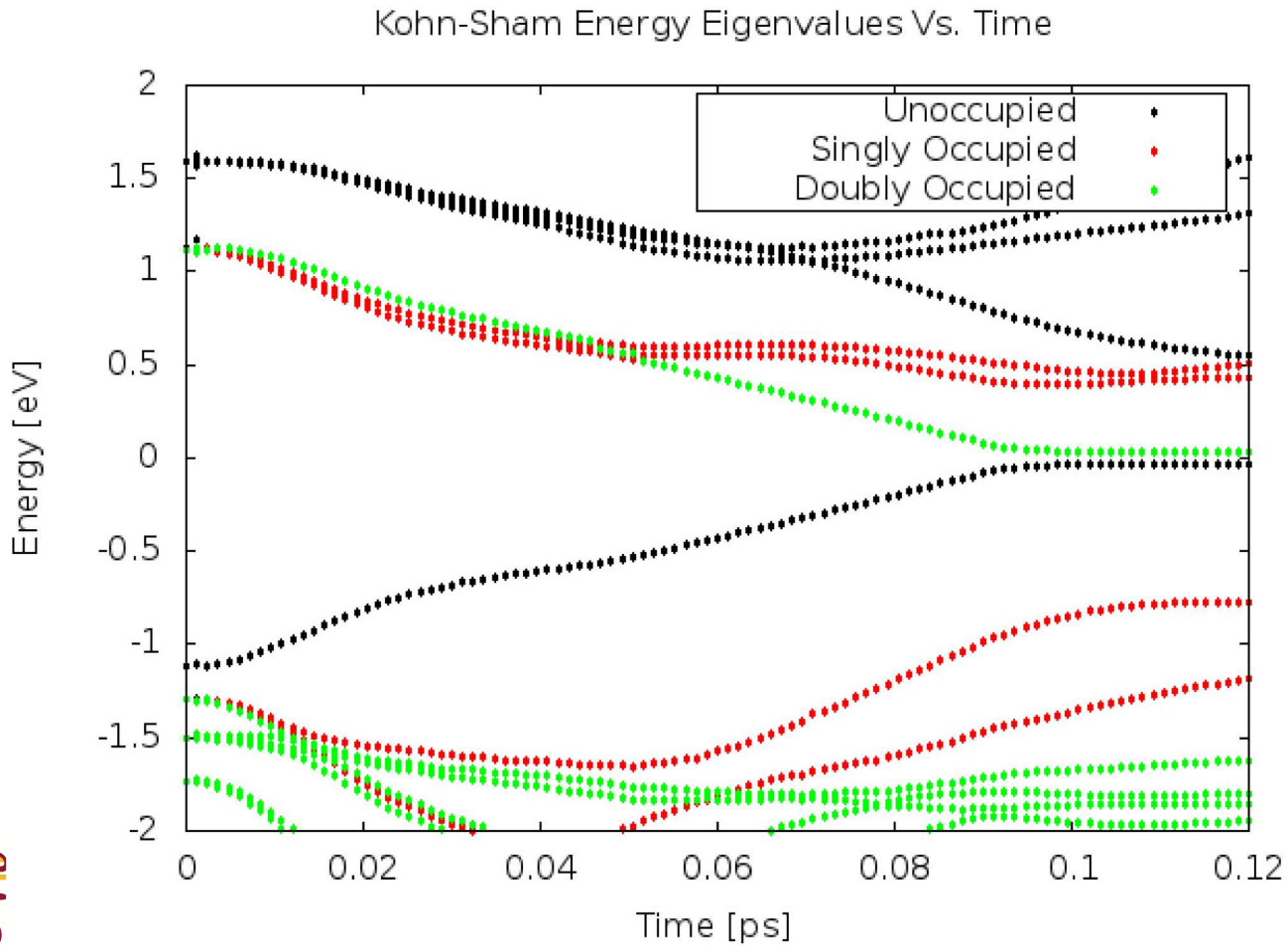
Hands-on: Visualize Data - Eigenenergies

Energies and occupations of the electronic bands, as a function of time, after simulating photoexcitation a 2x2x1 supercell of monolayer $MoSe_2$.



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