RIXS and exciton plotting

OCEAN : NSLS-II & CFN UM 2019, Hands-on session 3

Outline

- RIXS calculation
  - Steps needed
  - Example using diamond
- Exciton plotting
- Details of GMRES

Get the calculation running

- Go to session3/diamond
- Run the script diamond.sh
  - $ sbatch ./diamond.sh

- We'll look at this script shortly

RIXS review

- Coherent process, break into steps

1) Absorption
2) Core-level excitonic interactions
3) Emission
4) Valence-level excitonic interactions

RIXS review

- $$\sigma(\omega_1,\omega_2) \propto \sum_f \left| \sum_m \frac{\langle f|\hat{d}_2^\dagger|m\rangle\langle m|\hat{d}_1|i\rangle}{\varepsilon_m - \omega_1} \right|^2 \delta(\varepsilon_f + \omega_2 - \omega_1)$$

$$\sigma(\omega_1,\omega_2) \propto \sum_f \left| \langle f|\hat{d}_2^\dagger \left[\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \right] \hat{d}_1|i\rangle \right|^2 \delta(E_f + \omega_2 - \omega_1)$$

RIXS review

- $\sigma(\omega_1, \omega_2) \propto \sum_f \left| \langle f | \hat{d}_2^\dagger \left[\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f + \omega_2 - \omega_1)$

- $|x(\omega_1)\rangle \equiv \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \hat{d}_1 |i\rangle$

- $\sigma(\omega_1, \omega_2) \propto -\mathrm{Im} \left[\langle x(\omega_1) | \hat{d}_2 \left(\frac{1}{\omega_1 - \omega_2 - \hat{H}_{\mathrm{BSE}}^{val}} \right) \hat{d}_2^\dagger | x(\omega_1) \rangle \right]$

RIXS review

- $\sigma(\omega_1, \omega_2) \propto \sum_f \left| \langle f | \hat{d}_2^\dagger \left[\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \right] \hat{d}_1 | i \rangle \right|^2 \delta(E_f + \omega_2 - \omega_1)$

- $|x(\omega_1)\rangle \equiv \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \hat{d}_1 |i\rangle$

- $\sigma(\omega_1, \omega_2) \propto -\mathrm{Im} \left[\langle x(\omega_1) | \hat{d}_2 \left(\frac{1}{\omega_1 - \omega_2 - \hat{H}_{\mathrm{BSE}}^{val}} \right) \hat{d}_2^\dagger | x(\omega_1) \rangle \right]$

RIXS: Absorption and core-level exciton

- $|x(\omega_1)\rangle \equiv \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \hat{d}_1 |i\rangle$

- $|x(\omega_1)\rangle = \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} |e, \alpha\rangle\langle e, \alpha|\hat{d}_1|i\rangle$

  - *e* are the DFT conduction bands
  - α are the core-level orbitals
  - d_1 is the absorption operator

RIXS review: Emission

- $$\sigma(\omega_1, \omega_2) \propto -\mathrm{Im}\left[\langle x(\omega_1)|\hat{d}_2\left(\frac{1}{\omega_1 - \omega_2 - \hat{H}^{val}_{\mathrm{BSE}}}\right)\hat{d}_2^{\dagger}|x(\omega_1)\rangle\right]$$

RIXS review: Emission

- $$\sigma(\omega_1, \omega_2) \propto -\mathrm{Im}\left[\langle x(\omega_1)|\hat{d}_2\left(\frac{1}{\omega_1 - \omega_2 - \hat{H}^{val}_{\mathrm{BSE}}}\right)\boxed{\hat{d}_2^{\dagger}|x(\omega_1)\rangle}\right]$$

- $$\hat{d}_2^{\dagger}|x(\omega_1)\rangle = |e'', h\rangle\langle e'', h|\hat{d}_2^{\dagger}|e', \alpha'\rangle\langle e', \alpha'|\underbrace{\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1}|e, \alpha\rangle\langle e, \alpha|\hat{d}_1|i\rangle}_{|x(\omega_1)\rangle}$$

  - *e* are the DFT conduction bands
  - *h* are the DFT valence bands
  - α are the atomic core levels
  - d_2 is the emission operator

RIXS review: Emission and valence exciton

- $$\sigma(\omega_1, \omega_2) \propto -\mathrm{Im}\left[\langle x(\omega_1)|\hat{d}_2\left(\frac{1}{\omega_1 - \omega_2 - \hat{H}^{val}_{\mathrm{BSE}}}\right)\hat{d}_2^{\dagger}|x(\omega_1)\rangle\right]$$

RIXS review

- Coherent process, break into steps

1) Absorption & core-level excitonic interactions
2) Emission
3) Valence-level excitonic interactions

- Now we'll walk through how OCEAN works
  - Using the diamond example

Step 1: Absorption

- For XAS each site is independent
- But RIXS requires a coherent sum over all
  - No core hole in the final state

$$|x_\alpha(\omega_1)\rangle = \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1}|e,\alpha\rangle\langle e,\alpha|\hat{d}_1|i\rangle$$

  - Calculate $|x(\omega_1)\rangle = \sum_\alpha |x_\alpha(\omega_1)\rangle$
    - For our example we have 2 carbon sites

Step 1: Absorption

- Need to choose energies or energy range (also polarization)
  - Match experimental data
  - Pick out features from XAS

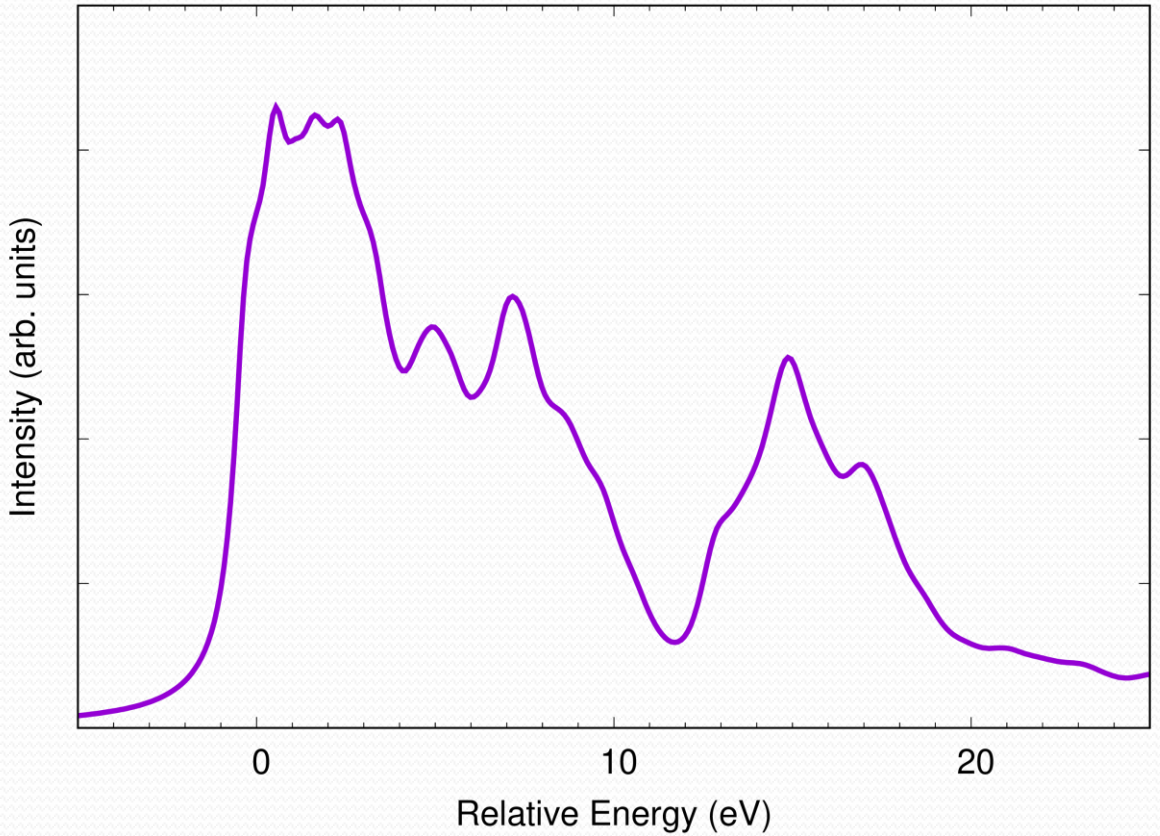
- Step 0: Run an XAS calculation

Step 0: XAS

- Run and plot absorption calculation
- From within diamond example
  - $ gnuplot
  - p ‘CNBSE/absspct_C_.0001_1s_01’ w l

Step 0: XAS

- Run and plot absorption calculation
- From within diamond example
  - $ gnuplot
  - p ‘CNBSE/absspct_C_.0001_1s_01’ w l
- This energy axis is what is used for calculating the excitons
  - Usually starting around 0 eV



Step 1: Absorption

- We have calculated the XAS
  - CNBSE/absspct …
- Now we want the XAS excitons
  1) Create directory RIXS
  2) Specify the energies
  3) Change BSE solver from Haydock to GMRES
  - The script diamond.sh does this for us

Absorption & Core-level exciton

- $|x(\omega_1)\rangle \equiv \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \hat{d}_1 |i\rangle$

- |*x*> are the excitons
  - Not single BSE eigenstate
  - Function of incoming energy
  - (also polarization & momentum)

Step 1: Absorption

- Need to decide which energies, polarizations, momenta
- Polarization & momentum are controlled by the photon files
- Two options for energies:

1) cnbse.gmres.elist
   - Manually list the energies
   - Useful for feature selection
2) cnbse.gmres.erange
   - Regularly spaced energies, i.e., RIXS map

Step 1: Absorption

- Two options for energies:

1) cnbse.gmres.elist
   - List of energy points (one energy per line)
2) cnbse.gmres.erange
   - Start energy; Stop energy; Energy spacing

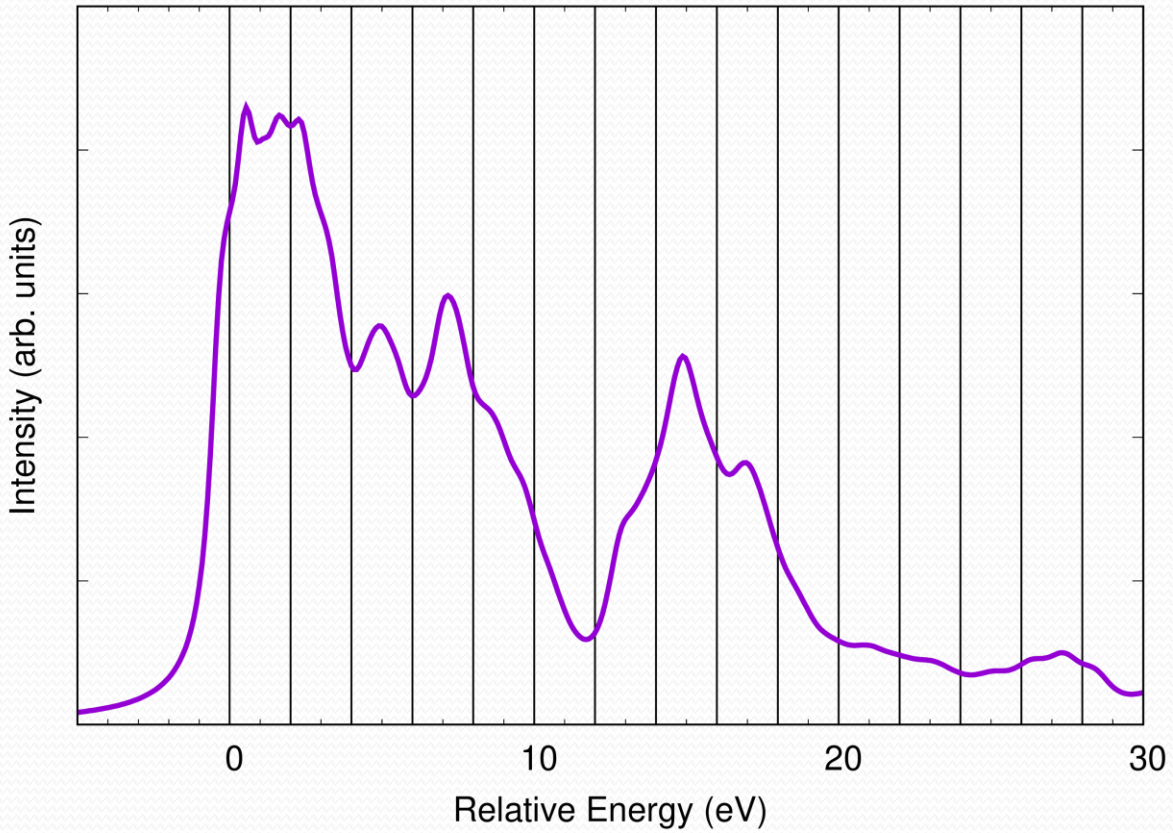
- Only one should be set! Erange takes priority

- In diamond.sh cnbse.gmres.erange is set

Step 1: Absorption

- In diamond.sh we set cnbse.gmres.erange
  - 0 30.1 2
  - 16 energies, starting at 0

    ending at 30



Absorption & Core-level exciton

- $|x(\omega_1)\rangle \equiv \frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1} \hat{d}_1 |i\rangle$

- Written as echamp_C_.0002_1s_01.0010
  - Chemical symbol
  - Index (2nd carbon in the cell)
  - Core level (1s)
  - XAS photon file (1st)
  - Energy iteration (10th energy or 18 eV)

RIXS steps

- Coherent process, break into steps

1) Absorption & core-level excitonic interactions
2) Emission
   - Need transition between valence and core
3) Valence-level excitonic interactions

Step 2: Emission

- $$\sigma(\omega_1, \omega_2) \propto -\mathrm{Im}\left[\langle x(\omega_1)|\hat{d}_2\left(\frac{1}{\omega_1 - \omega_2 - \hat{H}^{val}_{\mathrm{BSE}}}\right)\hat{d}_2^{\dagger}|x(\omega_1)\rangle\right]$$

- $$\hat{d}_2^{\dagger}|x(\omega_1)\rangle = |e'', h\rangle\langle e'', h|\hat{d}_2^{\dagger}|e', \alpha'\rangle\langle e', \alpha'|\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1}|e, \alpha\rangle\langle e, \alpha|\hat{d}_1|i\rangle$$

  - *e* are the DFT conduction bands
  - *h* are the DFT valence bands
  - α are the atomic core levels
  - d_2 is the emission operator

Step 2: Emission

- $\hat{d}_2^\dagger|x(\omega_1)\rangle = |e'', h\rangle\langle e'', h|\hat{d}_2^\dagger|e', \alpha'\rangle\langle e', \alpha'|\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega_1}|e, \alpha\rangle\langle e, \alpha|\hat{d}_1|i\rangle$

- $\langle e'', h|\hat{d}_2^\dagger|e', \alpha'\rangle = \langle e''|e'\rangle\langle h|\hat{d}_2^\dagger|\alpha\rangle$

- Electron stays the same
- Hole now in valence band

RIXS steps

- Coherent process, break into steps

1) Absorption & core-level excitonic interactions
2) Emission
3) Valence-level excitonic interactions

Step 3: Valence-level excitonic interactions

- Run another set of BSE calculations, but now for valence
- Transition matrix elements differ
  - $|e,h\rangle\langle e,h|e^{i\mathbf{q}\cdot\mathbf{r}}|i\rangle$
  - $\hat{d}_2^\dagger|x(\omega_1)\rangle = |e'',h\rangle\langle e'',h|\hat{d}_2^\dagger|e',\alpha'\rangle\langle e',\alpha'|\frac{1}{\hat{H}_{\mathrm{BSE}}-\omega_1}|e,\alpha\rangle\langle e,\alpha|\hat{d}_1|i\rangle$
    - Code automatically sums over the sites α

Step 3: Valence-level excitonic interactions

- Results are RIXS/rxsspct_C_.1s_02.00014.01
  - Element symbol (C_)
  - Core level (1s)
  - Incoming x-ray photon file (02)
  - Energy step index (14)
  - Out-going photon file (01)
- No atomic site! We sum over all of them
- Two different photon files

Step 3: Valence-level excitonic interactions

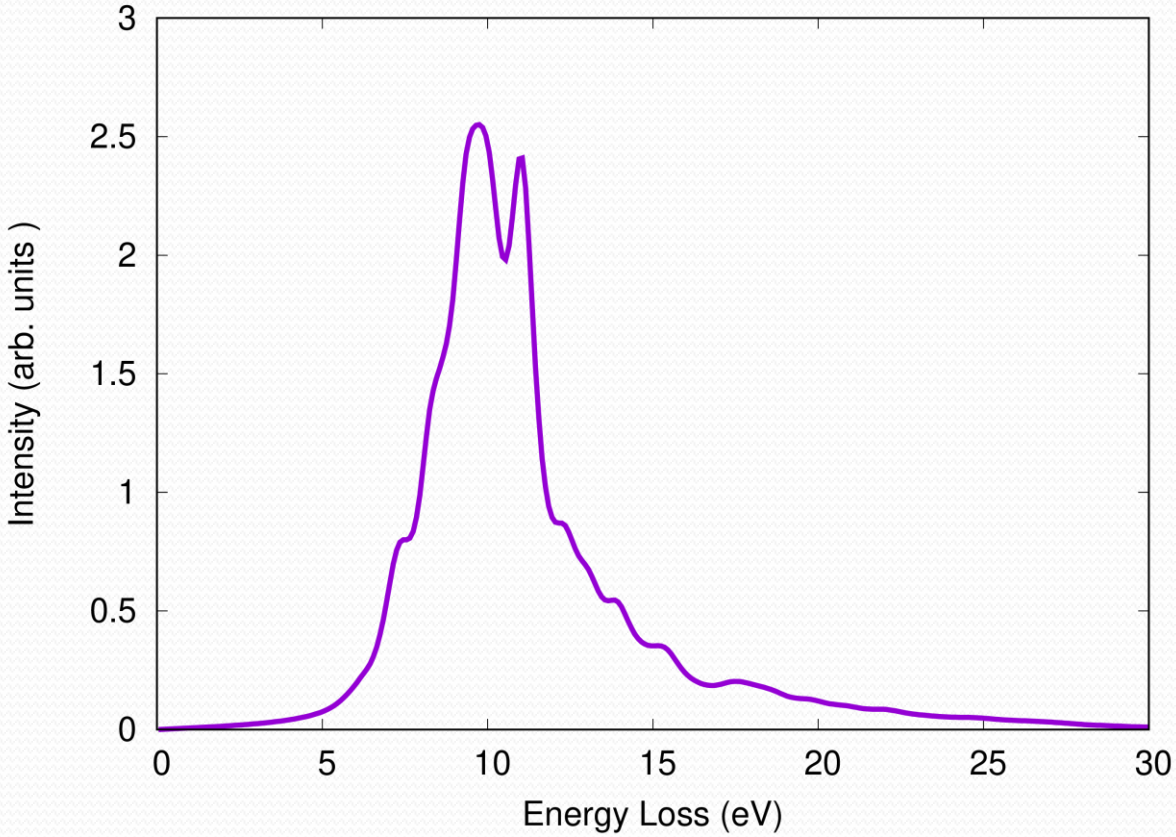
- $\sigma(\omega_1, \omega_2) \propto -\mathrm{Im}\left[\langle x(\omega_1)|\hat{d}_2\left(\frac{1}{\omega_1 - \omega_2 - \hat{H}^{val}_{\mathrm{BSE}}}\right)\hat{d}_2^{\dagger}|x(\omega_1)\rangle\right]$

- Spectra are with respect to energy loss: $\omega_1 - \omega_2$

- Open gnuplot
  - p ‘RIXS/rxsspct_C_.1s_01.00001.02' u 1:3 w l
  - Columns 1 & 3!

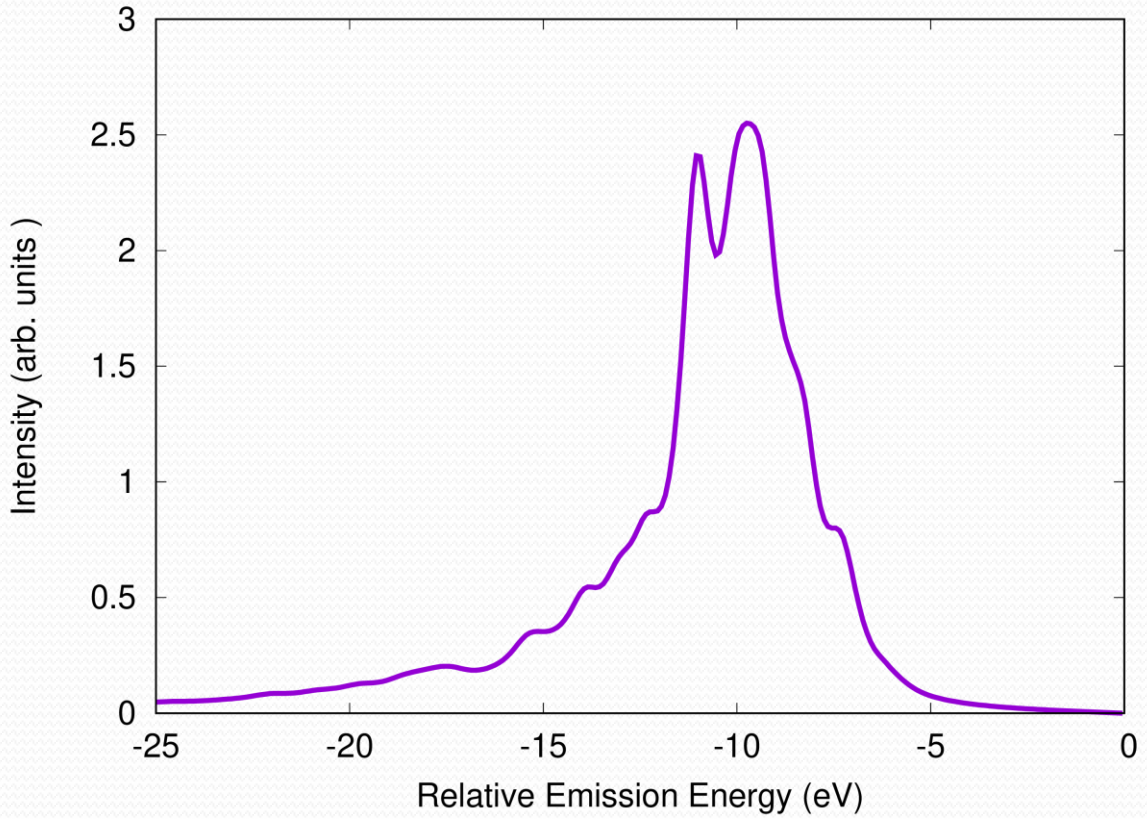
Step 3: Valence-level excitonic interactions

- p ‘RIXS/rxsspct_C_.1s_01.00001.02' u 1:3 w l
  - Columns 1 & 3!



Step 3: Valence-level excitonic interactions

- Plot versus emission energy
- p ‘RIXS/rxsspct_C_.1s_01.00001.02’ u (0-$1):3 w l
  - The XAS energy was at 0 eV
  - (Absorption is still in terms of relative energies)



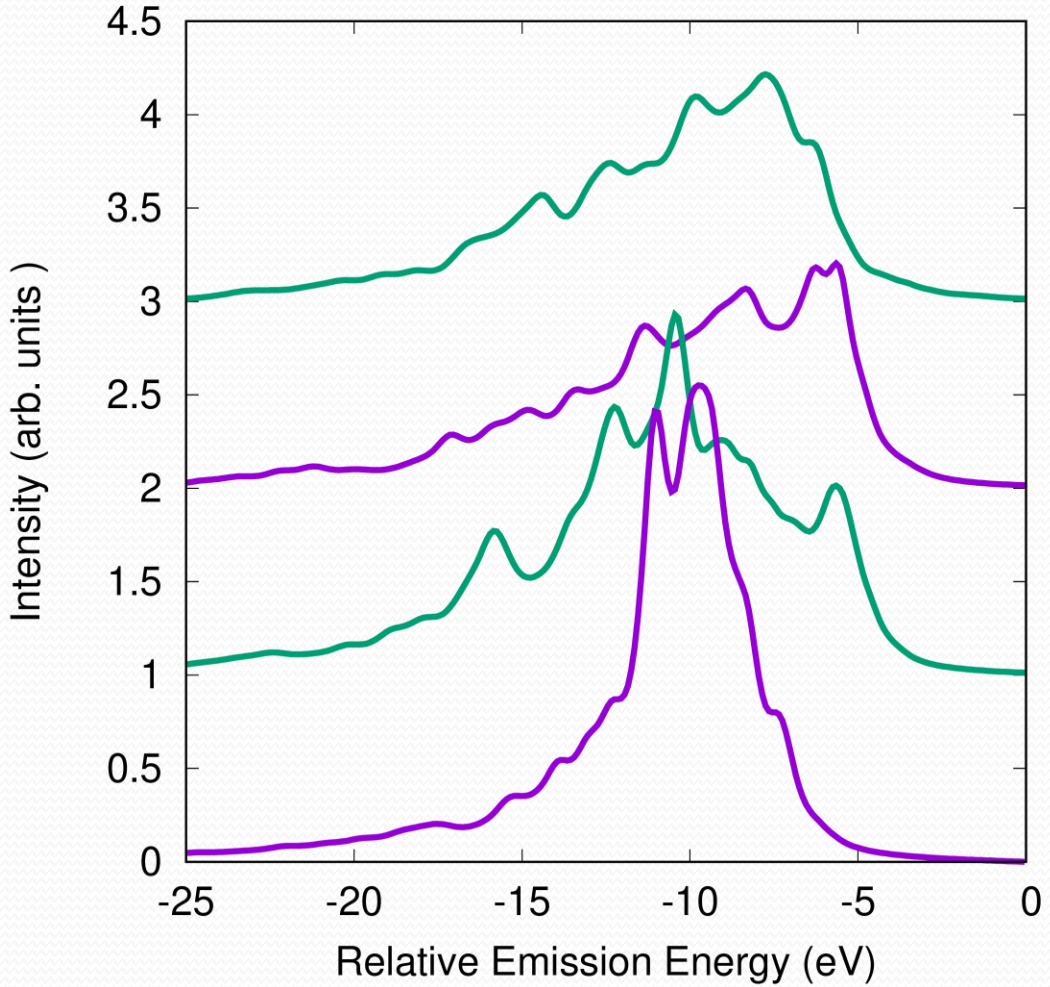
Step 3: Valence-level excitonic interactions

- Plot first four spectra
  - Initial XAS changes by 2 eV each step
  - Column 1 is energy loss
  - Plots are offset vertically from each other
- ‘rxsspct_C_.1s_01.00001.02’ u (0-$1):3 w l,

‘rxsspct_C_.1s_01.00002.02’ u (2-$1):($3+1) w l,

‘rxsspct_C_.1s_01.00003.02’ u (4-$1):($3+2) w l,

‘rxsspct_C_.1s_01.00004.02’ u (6-$1):($3+3) w l



RIXS Recap

- Look at diamond.sh
- $OCEAN_BIN/ocean.pl diamond.in
  - Runs the XAS (Step 0)
  - Ordinarily run XAS alone to figure out convergence

RIXS Recap

- Look at diamond.sh
- $OCEAN_BIN/ocean.pl diamond.in
- echo gmres > Common/cnbse.solver
  - Switch cnbse.solver from Haydock to GMRES
  - Haydock gives spectrum (Lanczos-like algorithm)
  - We'll come back to GMRES settings shortly

RIXS Recap

- Look at diamond.sh
- $OCEAN_BIN/ocean.pl diamond.in
- echo gmres > Common/cnbse.solver
- echo 1 > RIXS/photon_in ; echo 2 > RIXS/photon_out
  - Select incident and emitted photon information (can be lists)
  - By default rixs.pl will run every pair of photon files (excluding repeats)
  - The correct pairings depends on geometry of measurement

RIXS Recap

- Look at diamond.sh
- $OCEAN_BIN/ocean.pl diamond.in
- echo gmres > Common/cnbse.solver
- echo 1 > RIXS/photon_in ; echo 2 > RIXS/photon_out
- $OCEAN_BIN/rixs.pl
  - Script that runs steps of RIXS calculation

Outline

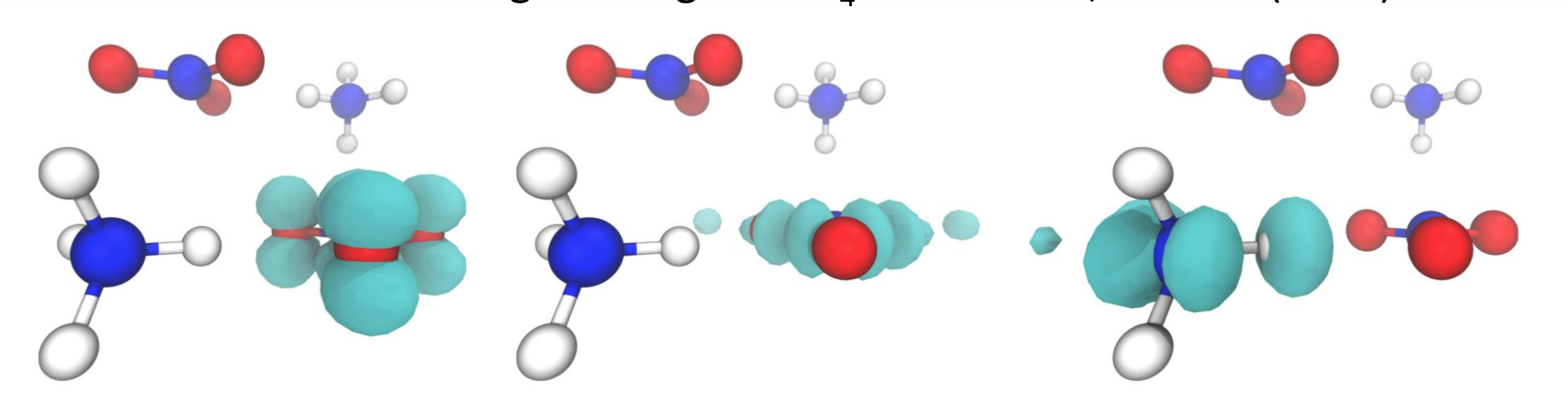
- RIXS calculation
- Exciton plotting
- Details of GMRES

Exciton Plotting: Example LiF

- Start the example running
- $ cd session3/LiF_exciton
- sbatch xrs.haydock

Exciton Plotting

- Want to visualize the electron density of an excitation
  - Need to solve BSE to get exciton wavefunction
  - Standard Haydock (Lanczos) routine only gives spectrum
- Ex: Excitons at the nitrogen K edge in NH_4NO3 PRB **94**, 035163 (2016)



Exciton Plotting

- Use same process as for RIXS
  - Use GMRES to solve for |x>
  - Exciton as coefficients of electron and hole states

$$|x(\omega)\rangle = |e,\alpha\rangle\langle e,\alpha|\frac{1}{\hat{H}_{\mathrm{BSE}} - \omega}|e',\alpha'\rangle\langle e',\alpha'|\hat{d}|i\rangle$$

$$|x(\omega)\rangle = \sum_{e,\alpha} |e,\alpha\rangle C_{e,\alpha}$$

Exciton Plotting

- Exciton has two sets of coordinates: electron & hole
  - Need to fix one for plotting
  - For core levels hole isn't interesting
- OCEAN uses band-structure picture
  - $|e\rangle = |n\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$
  - Need to go to real space
  - Not novel: c.f., Olovsson *et al.*, PRB **83**, 195206 (2011)

Exciton Plotting

- $|x(\omega)\rangle = \sum_{e,\alpha} |e,\alpha\rangle C_{e,\alpha}$

- $x(\mathbf{x},\mathbf{x}',\mathbf{k},\mathbf{q};\omega) = \sum_{n,\mathbf{k},\alpha} C_{n,\mathbf{k},\alpha}\, e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{x}'} u_{n,\mathbf{k}}(\mathbf{x}) \chi_{\alpha}(\mathbf{x}')$

  - Electron and hole are offset by photon momentum **q**
  - Center **x'** at the absorbing atom

Exciton Plotting

- $|x(\omega)\rangle = \sum_{e,\alpha} |e,\alpha\rangle C_{e,\alpha}$

- $x(\mathbf{x},\mathbf{x}',\mathbf{k},\mathbf{q};\omega) = \sum_{n,\mathbf{k},\alpha} C_{n,\mathbf{k},\alpha}\, e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{x}'} u_{n,\mathbf{k}}(\mathbf{x}) \chi_{\alpha}(\mathbf{x}')$
  - Electron and hole are offset by photon momentum **q**
  - Center **x'** at the absorbing atom
- $x(\mathbf{x},\mathbf{k};\omega) = \sum_{n,\mathbf{k},\alpha} C_{n,\mathbf{k},\alpha}\, e^{i\mathbf{k}\cdot\mathbf{x}} u_{n,\mathbf{k}}(\mathbf{x})$

Exciton Plotting

- $x(\mathbf{x}, \mathbf{k}; \omega) = \sum_{n,\mathbf{k},\alpha} C_{n,\mathbf{k},\alpha}\, e^{i\mathbf{k}\cdot\mathbf{x}} u_{n,\mathbf{k}}(\mathbf{x})$

- $x(\mathbf{x}, \mathbf{R}; \omega) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{n,\mathbf{k},\alpha} C_{n,\mathbf{k},\alpha}\, e^{i\mathbf{k}\cdot\mathbf{x}} u_{n,\mathbf{k}}(\mathbf{x})$

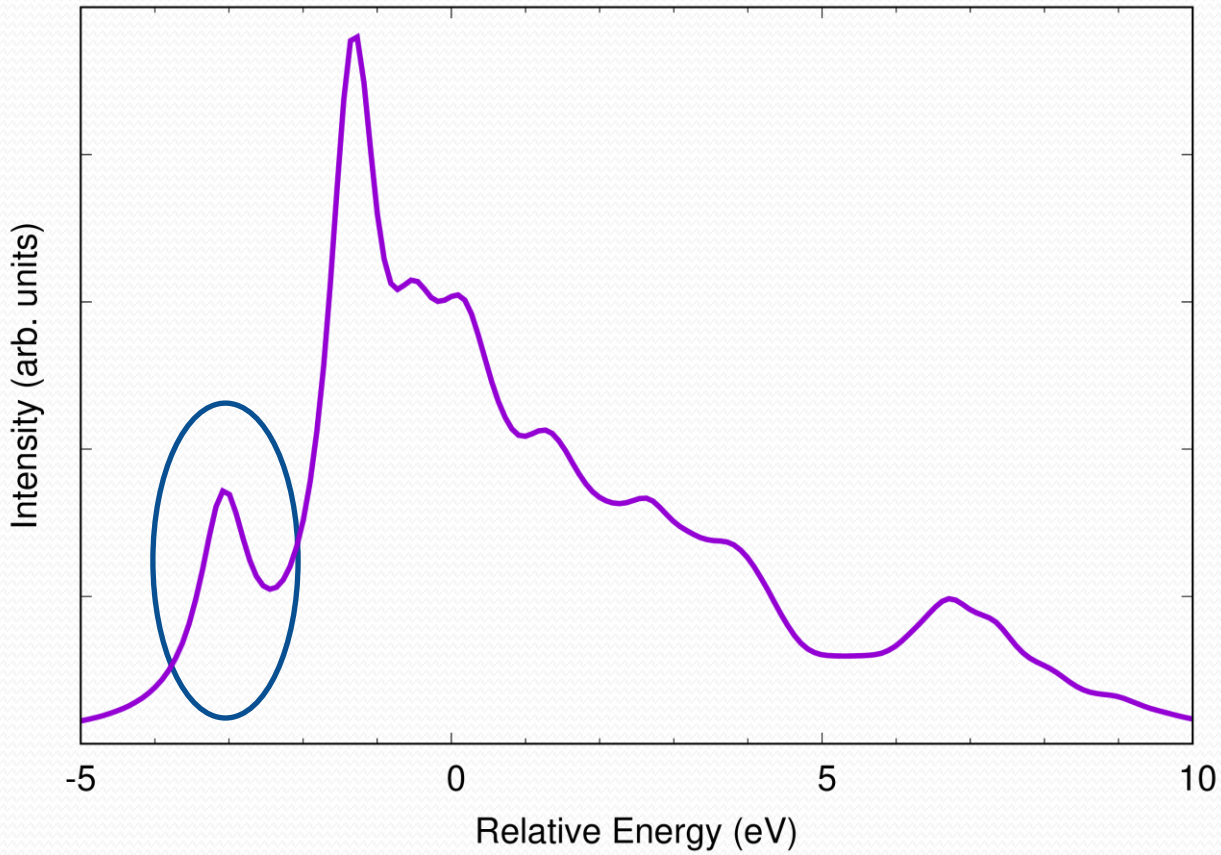
  - Fourier transform to super cells
  - Excitation localized – only need a few neighboring cells

Exciton Plotting

- $x(\mathbf{x}, \mathbf{R}; \omega) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{n,\mathbf{k},\alpha} C_{n,\mathbf{k},\alpha} e^{i\mathbf{k}\cdot\mathbf{x}} u_{n,\mathbf{k}}(\mathbf{x})$
- CNBSE/echamp file
- OCEAN-style DFT orbitals (CNBSE/u2.dat)
  - Uses same x-mesh grid

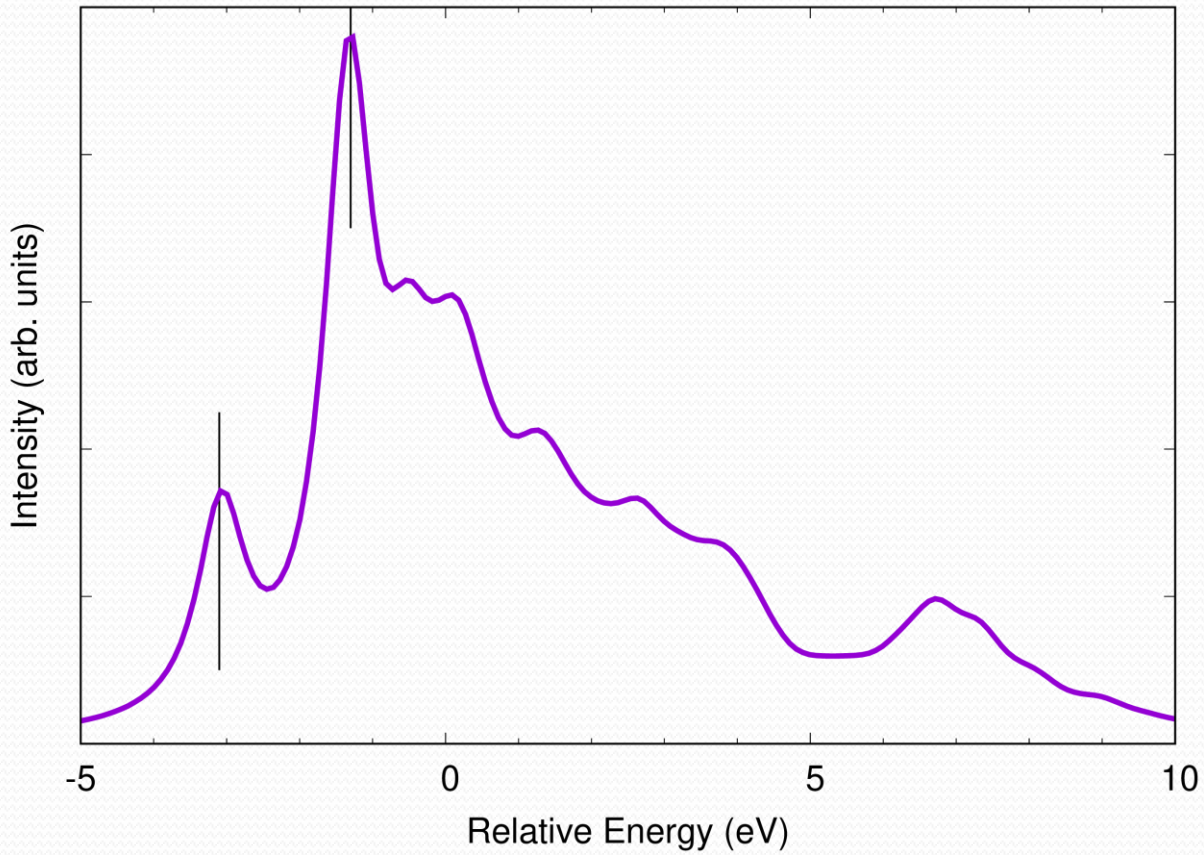
Exciton Plotting: LiF example

- Look at fluorene K-edge
- NRIXS shows q-dependent pre-edge feature
- Plot CNBSE/absspct_F_.0001 _1s_01



Exciton Plotting: LiF example

- Look at fluorene K-edge
- NRIXS shows q-dependent pre-edge feature
- Plot CNBSE/absspct_F_.0001 _1s_01
- Compare excitons at pre-edge and main edge
  - -3.1 eV & -1.3 eV (relative)
- $ sbatch xrs.gmres



Exciton Plotting: LiF example

- Script xrs.gmres does the following:

- Sets Common/cnbse.solver to gmres
- Sets Common/cnbse.gmres.elist
  -3.1
  -1.3
- Makes new directory GMRES
- Adds echamp.inp .true. (inside GMRES)
- Re-runs cnbse_mpi.pl (in GMRES)
  - Runs core-level BSE
  - Generates absspct and echamp files
  - Only for energies specified in cnbse.gmres.elist (or cnbse.gmres.erange)

Exciton Plotting: LiF example

- Exciton plot program has a simple input
- Edit exciton_plot.ipt (in GMRES)

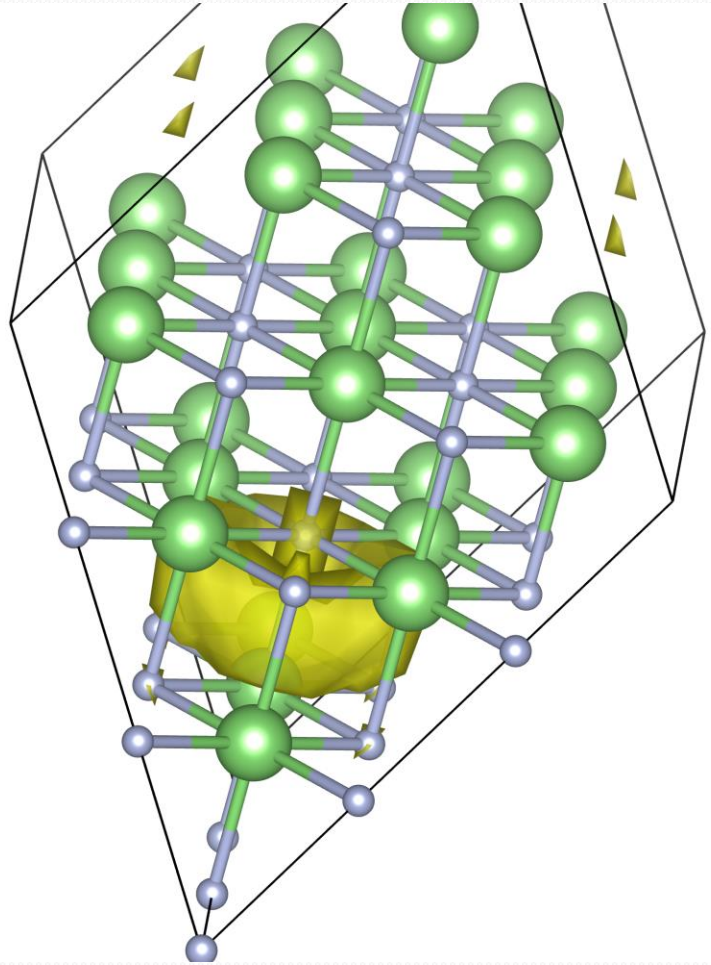
```
echamp_F_.0001_1s_01.0001
e1.cube
3 3 3
-1 -1 -1
```

  - Input
  - Output
  - Supercell size
  - Supercell origin

- Run plot routine in GMRES directory
  - /hpcgpfs01/work/workshop/ocean_tutorial/bin/exciton_plot.x

Exciton Plotting: LiF example

- Output is in Gaussian cube format
- Can use VESTA to visualize it
  - http://jp-minerals.org/vesta/en/
  - Other programs work too

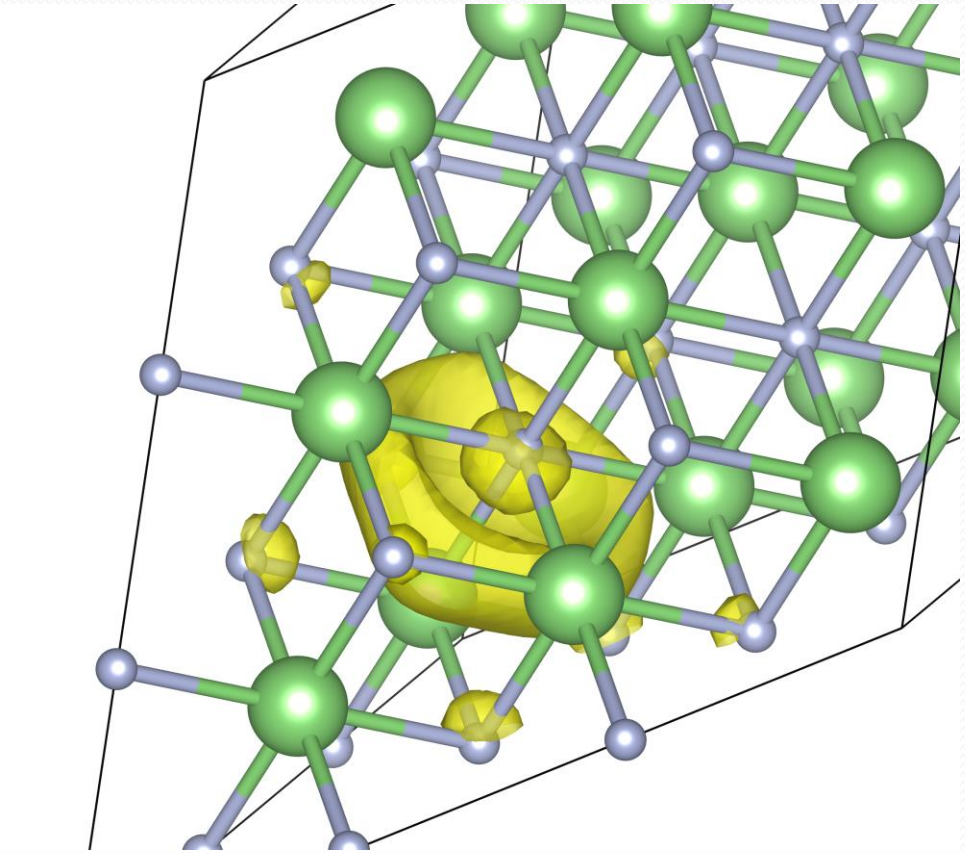


Exciton Plotting: LiF example

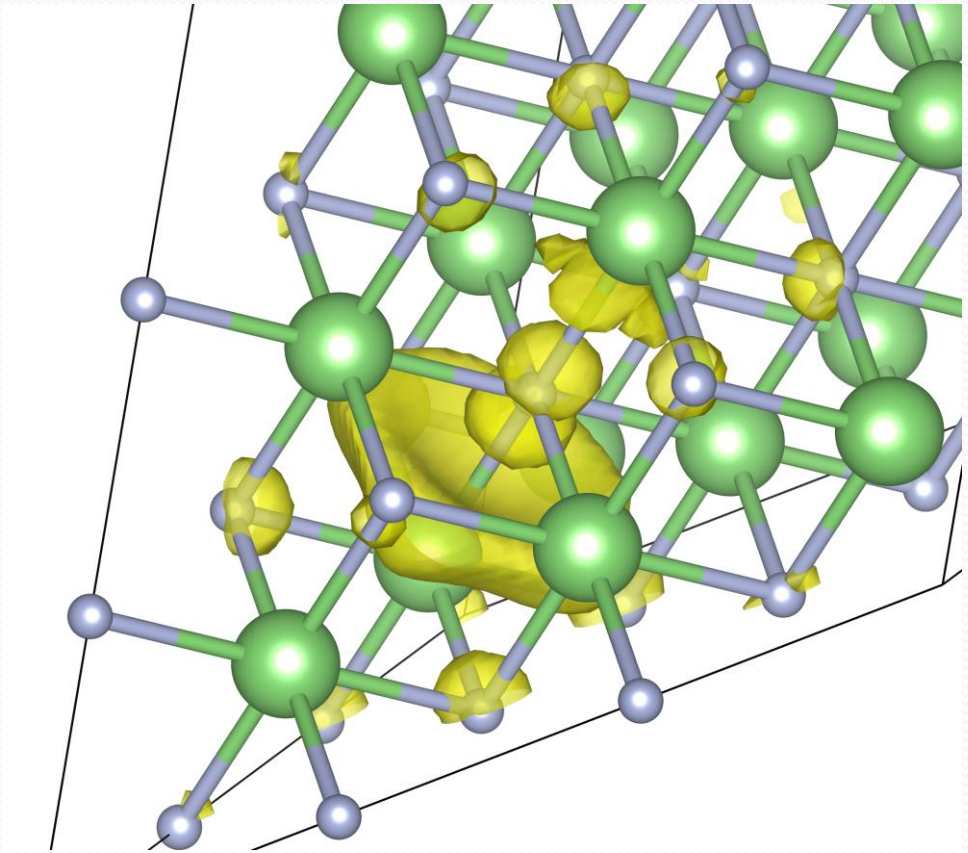
- Grid set by initial BSE calculation
  - 4x4x4 per unit cell
- Increase the quality
  - Don’t need to re-run the BSE
- Within the GMRES directory
  - unlink u2.dat
  - edit xmesh.ipt
  - run setup2.x, conugtoux.x, and then orthog.x
  - re-run exciton_plot.x

Exciton Plotting: LiF example

- Pre-edge



- Main edge



end