Practical BSE Calculations with BerkeleyGW

Felipe H. da Jornada

Department of Physics – University of California, Berkeley
and Lawrence Berkeley National Laboratory
BerkeleyGW Workshop – Nov. 23rd , 2013

Summary

- Practical BSE Calculations

  #1 – Theoretical and methodological overview

  #2 – Typical BSE workflow in BerkeleyGW

  #3 – Issues unique to the BSE code

Summary

- Practical BSE Calculations

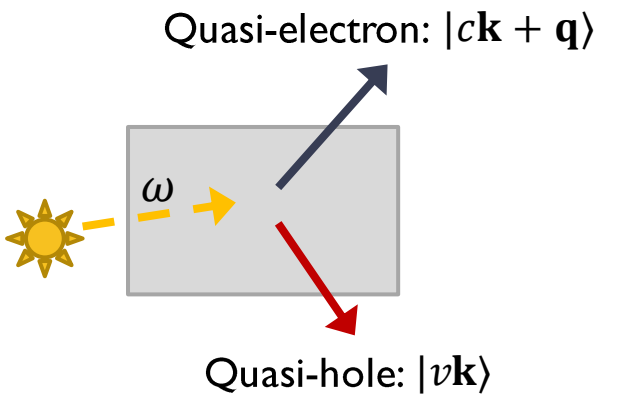
#1 – Theoretical and methodological overview

#2 – Typical BSE workflow in BerkeleyGW

#3 – Issues unique to the BSE code

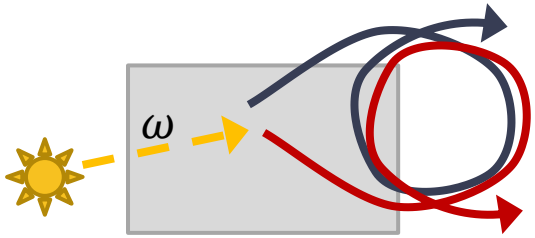
Theory Review: Optical Absorption

No electron-hole interactions



$$\varepsilon_2(\mathbf{q},\omega) \propto \sum_{vc\mathbf{k}} |\langle v\mathbf{k}|\hat{v}|c\mathbf{k}+\mathbf{q}\rangle|^2 \delta\left[\omega - \left(E_{c\mathbf{k}+\mathbf{q}} - E_{v\mathbf{k}}\right)\right]$$

With electron-hole interactions



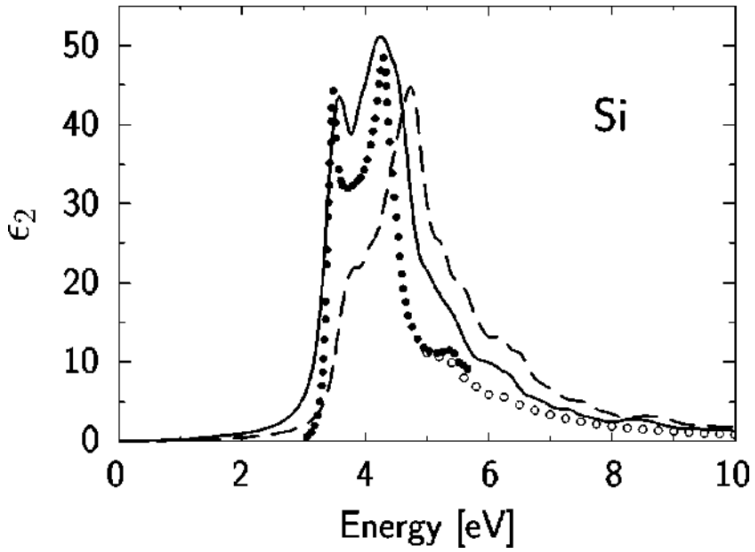
$$\varepsilon_2(\mathbf{q},\omega) \propto \sum_{S} |\langle 0|\hat{v}|S\rangle|^2 \delta[\omega - \Omega_S]$$

$$|S\rangle = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \, |v\mathbf{k}\rangle \otimes |c\mathbf{k}+\mathbf{q}\rangle$$

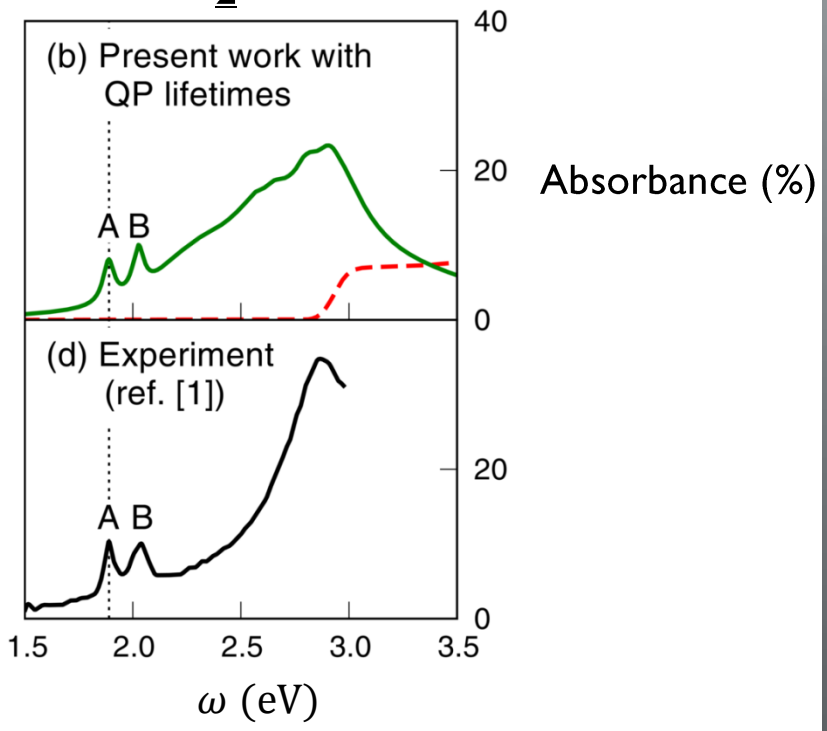
Solutions of the Bethe-Salpeter equation (BSE)

Optical Absorption Spectrum and Excitons

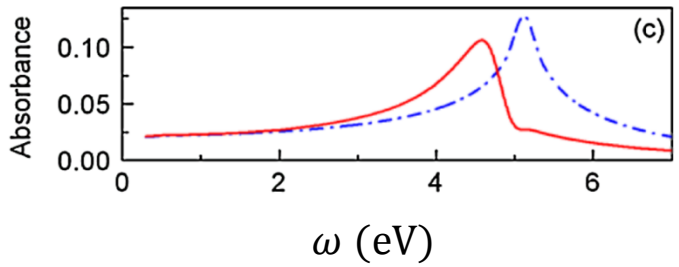
1. Silicon



2. MoS_2



3. Graphene



[1] M. Rohlfing, S. G. Louie, PRB **62**, 8 (2000).
[2] D. Qiu, F. H. da Jornada, S. G. Louie, PRL **111**, 216805 (2013).
[3] L. Yang, J. Deslippe, C.-H. Park, M. L. Cohen, and S. G. Louie, PRL **103**,186802 (2009).

Bethe Salpeter Equation (BSE)

- Absorption spectrum with excitonic effects → diagonalize BSE Hamiltonian:

$$[H]_{(vc\mathbf{k}),(v'c'\mathbf{k}')}$$

$$[H] = [E_c - E_v] + [K]$$

$[K]$ ← dense "kernel" ~ potential term

$[E_c - E_v]$ ← diagonal ~ kinetic term

Challenge: compute quasiparticle corrections and kernel matrix elements on a very fine k-grid!

BerkeleyGW Interpolation Scheme

BerkeleyGW solution:
Interpolate QP energies and BSE kernel

- Step 1: Expand fine WFNs in terms of coarse WFNs

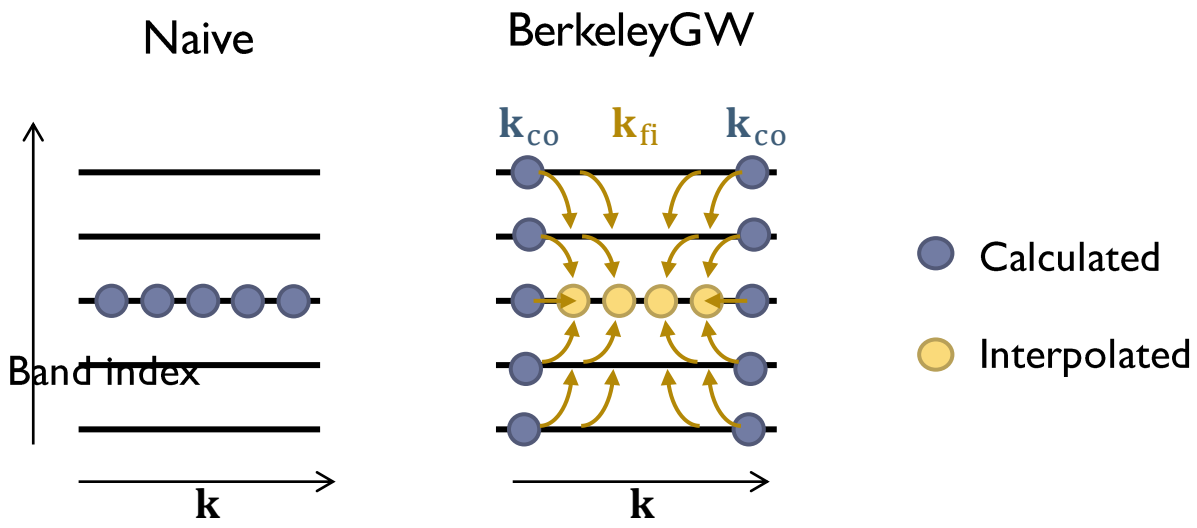
$$u_{n\mathbf{k}_{\mathrm{fi}}} = \sum_{n'} C^{\mathbf{k}_{\mathrm{co}}}_{n,n'} u_{n'\mathbf{k}_{\mathrm{co}}}$$

- Step 2: Interpolate QP energies and matrix elements

$$\langle vc\mathbf{k}_{\mathrm{fi}}|K|v'c'\mathbf{k}'_{\mathrm{fi}}\rangle = \sum_{n_1,n_2,n_3,n_4} C^{\mathbf{k}_{\mathrm{co}}}_{c,n_1} C^{*\mathbf{k}_{\mathrm{co}}}_{v,n_2} C^{*\mathbf{k}'_{\mathrm{co}}}_{c',n_3} C^{\mathbf{k}'_{\mathrm{co}}}_{v',n_4} \langle n_2 n_1 \mathbf{k}_{\mathrm{co}}|K|n_4 n_3 \mathbf{k}'_{\mathrm{co}}\rangle$$

BerkeleyGW Interpolation Scheme

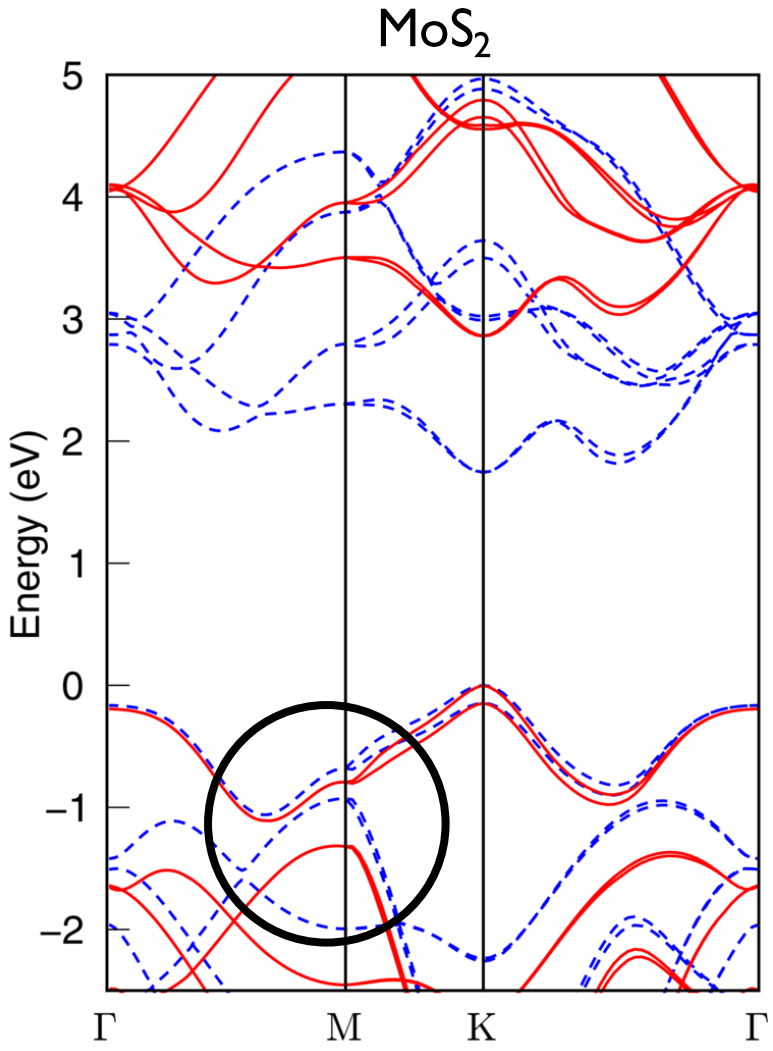
- In practice: trading bands for k-points



- How to get a good interpolation?
  - Include a large number of bands from the coarse grid!

BerkeleyGW QP Interpolation

- BerkeleyGW also performs a linear interpolation for QP corrections.
- Linear interpolation + expansion over bands:
  - Captures (n**k**)-dependent QP correction and band crossing
  - Very smooth interpolation of band structure
  - Robust scheme, and very few parameters
- This is how inteqp.x works!



D. Qiu, F. H. da Jornada, S. G. Louie, PRL **111**, 216805 (2013)

Summary

- Practical BSE Calculations

#1 – Theoretical and methodological overview

#2 – Typical BSE workflow in BerkeleyGW

#3 – Issues unique to the BSE code

BerkeleyGW Workflow

Goal: Diagonalize BSE Hamiltonian on a coarse grid

$$[H]_{\text{fi}} = [E_c - E_v]_{\text{fi}} + [K]_{\text{fi}}$$

BerkeleyGW Workflow

Step 1: Calculate QP–corrected band structure on a coarse grid

sigma.x

$$\{E_c\}_{\text{co}}, \{E_v\}_{\text{co}},$$

Step 2: Calculate BSE kernel on the same coarse grid

kernel.x

$$[K]_{\text{co}}$$

Step 3: Interpolate to a fine k-grid and build BSE Hamiltonian…

$$[H]_{\text{co}} \Rightarrow [H]_{\text{fi}}$$

… and diagonalize BSE Hamiltonian

absorption.x

$$\text{evals}\ [H]_{\text{fi}} \Rightarrow \varepsilon_2$$

1. Sigma

Step 1: Calculate QP–corrected band structure on a coarse grid

sigma.x

$\{E_c\}_{\text{co,}}\ \{E_v\}_{\text{co,}}$

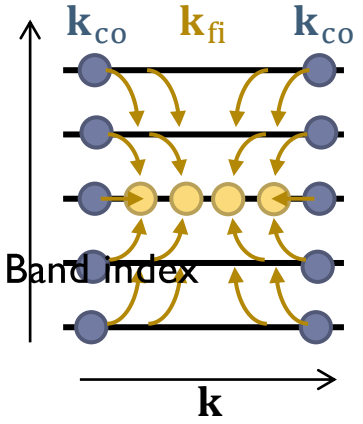
- Same procedure done in previous sessions.
- Recommended: eqp.dat
  - Calculate QP energies on all k-points from WFN_inner.
  - Use the script eqp.py to generate eqp.dat file → no human intervention!
- Also possible: scissors operators
  - Run a Sigma calculation on only a few k-points from WFN_inner.
  - Fit linear energy-dependent scissors operators → only ok for isotropic systems!

1. Sigma

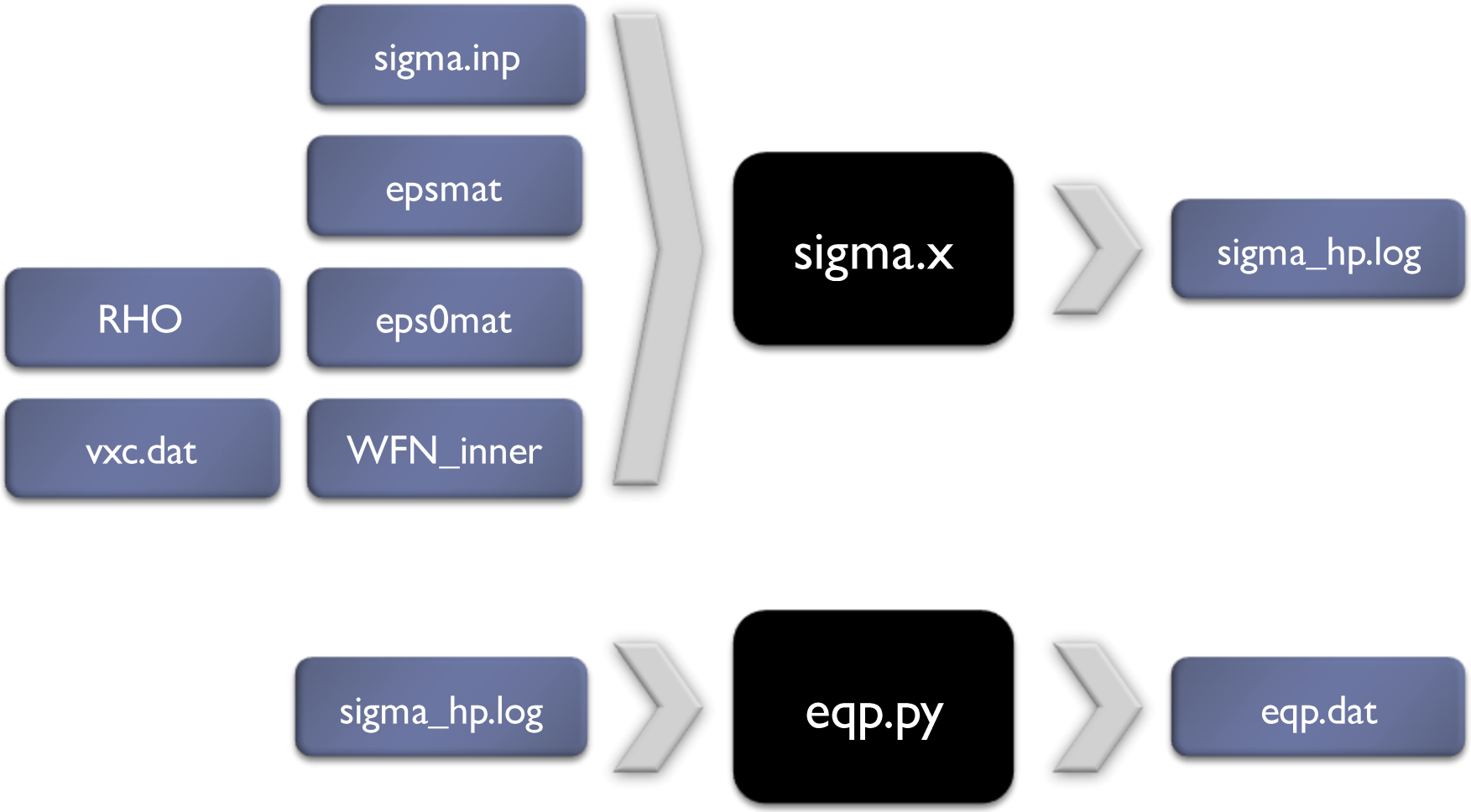
Sample sigma.inp (assuming we are using eqp.dat)

```
screened_coulomb_cutoff <?>
bare_coulomb_cutoff <?>

number_bands <?>
band_occupation <?>

band_index_min <?>
band_index_max <?>

screening_semiconductor
number_kpoints <?>
begin kpoints
 <put all k-points from WFN_INNER here>
end
```

Remember to calculate Sigma on more bands because of the interpolation!



1. Sigma – Workflow



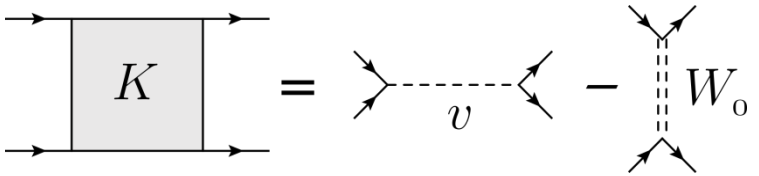
2. Kernel

Step 2: Calculate BSE kernel on the same coarse grid

kernel.x

$$[K]_{\mathrm{co}}$$

- Time consuming!
  - Computes $(n_v n_c n_k)^2$ matrix elements



bsexmat bsedmat

head, wing, body

- Recommended:
  - Use same WFN_co as in Sigma (WFN_inner)
- Also possible:
  - Use a different grid in WFN_co, only possible with scissors operators.

2. Kernel

Sample kernel.inp

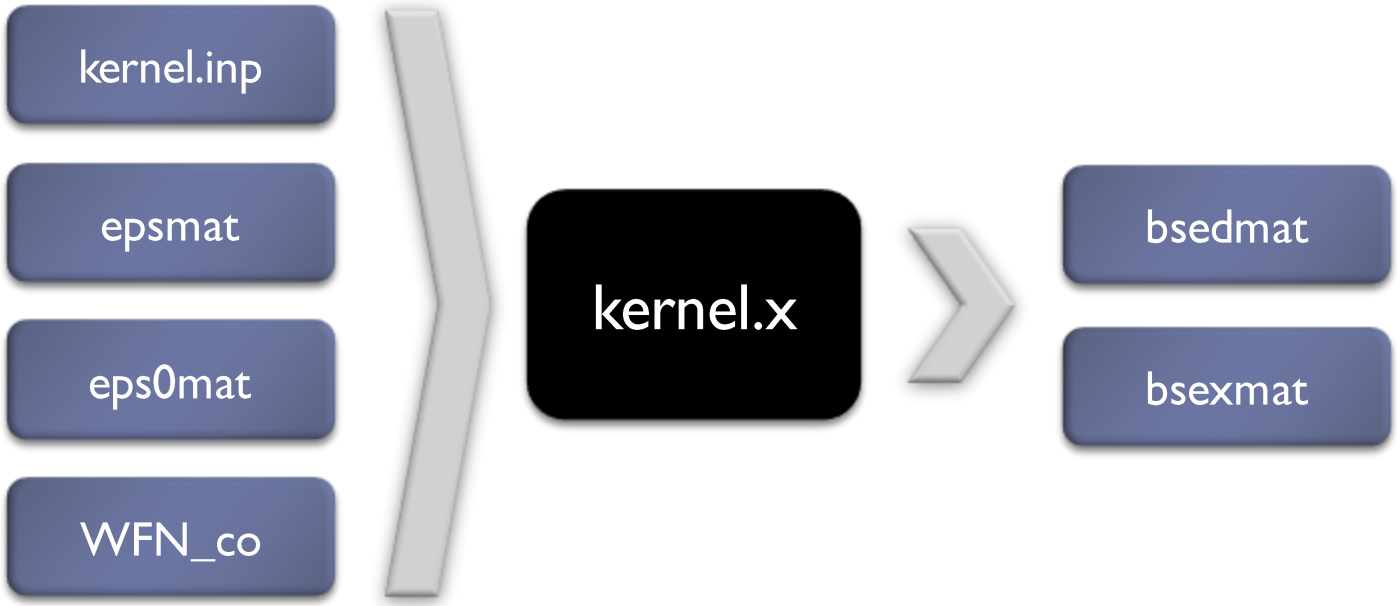
```
number_val_bands <?>
number_cond_bands <?>

screened_coulomb_cutoff <?>

<?>_symmetries_coarse_grid
screening_<?>
```

Remember to calculate Kernel on more bands because of the interpolation!

# of bands in Sigma can't be less than this number!

You'll typically want to use symmetries here, so put:
`use_symmetries_coarse_grid`

2. Kernel – Workflow



3. Absorption

Step 3: Interpolate to a fine k-grid and build BSE Hamiltonian…

$$[H]_{\mathrm{co}} \Rightarrow [H]_{\mathrm{fi}}$$

… and diagonalize BSE Hamiltonian

absorption.x

$$\mathrm{evals}\ [H]_{\mathrm{fi}} \Rightarrow \varepsilon_2$$

- Absorption needs same coarse WFN_co from Kernel/Sigma
- Absorption also need two fine WFN files:
  - WFN: for conduction states
  - WFNq: for valence states

- Good practice: use randomly-shifted k-grids
  - This maximized the number of transitions you are capturing.

3. Absorption

Sample absorption.inp

```
diagonalization

number_val_bands_coarse <?>
number_cond_bands_coarse <?>
number_val_bands_fine <?>
number_cond_bands_fine <?>

coarse_grid_points <?>

use_symmetries_coarse_grid
no_symmetries_fine_grid
no_symmetries_shifted_grid

screening_semiconductor

use_velocity
q_shift 0.0 0.0 0.001

gaussian_broadening
energy_resolution 0.15

eqp_co_corrections
```

Same as used in kernel.

We interpolate to these bands!

How many k-points in the coarse grid after unfolding BZ?

Typical values.

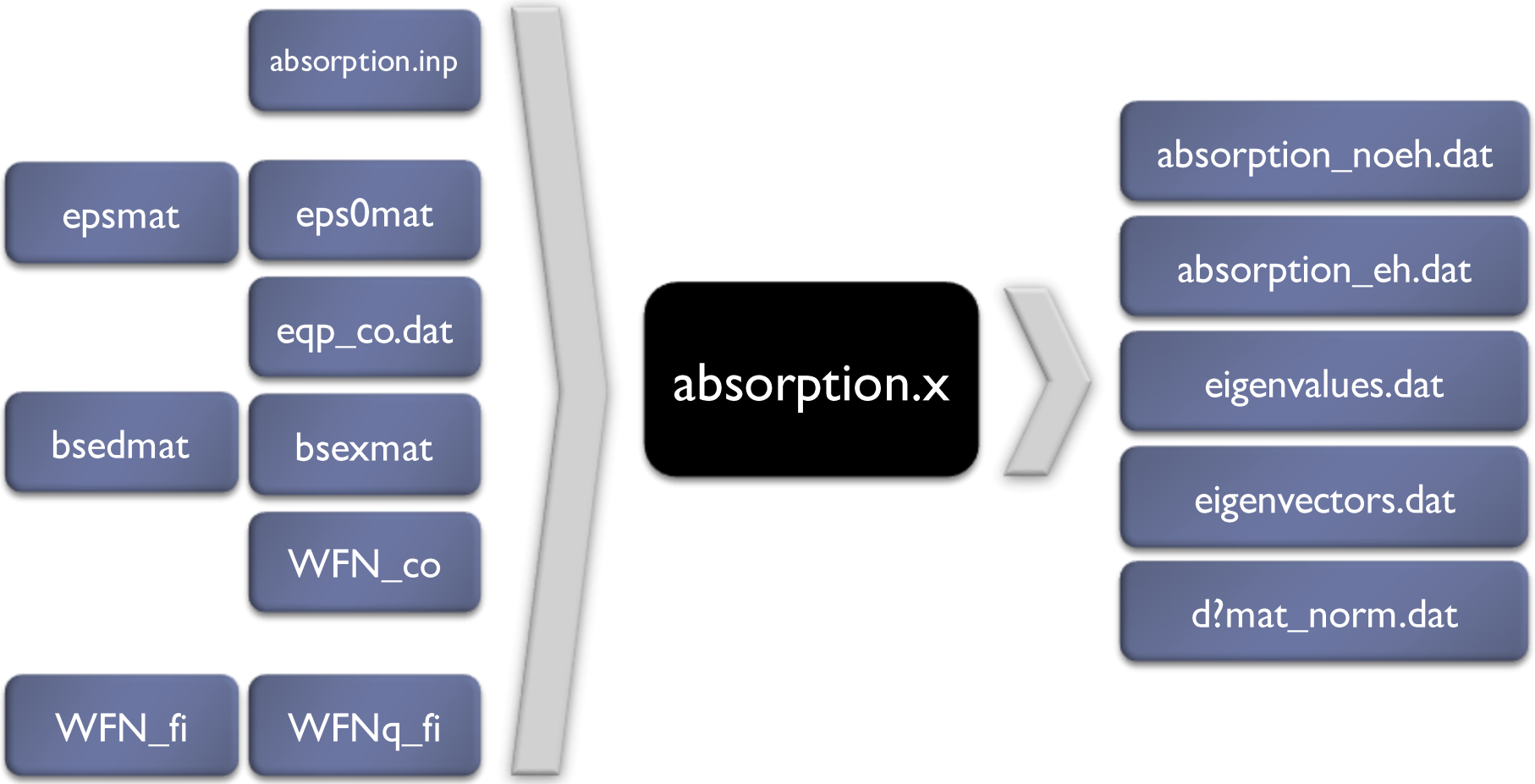
Recommended!

$\mathbf{k}_{\mathrm{WFN}} + \mathbf{q}_{\mathrm{shift}} = \mathbf{k}_{\mathrm{WFNq}}$

Broaden each delta function.

Interpolate eqp_co.dat

3. Absorption – Workflow



Summary

- Practical BSE Calculations

#1 – Theoretical and methodological overview

#2 – Typical BSE workflow in BerkeleyGW

#3 – Issues unique to the BSE code

Issues Unique to the BSE Code

1. Velocity operator
2. Number of converge knobs
3. Estimating the quality of the interpolation
4. Direct diagonalization vs. haydock
5. Analyzing exciton files

1. Velocity operator

$$\varepsilon_2(\mathbf{q},\omega) \propto \sum_S |\langle 0|\hat{v}|S\rangle|^2 \delta[\omega - \Omega_S] \qquad \langle 0|\hat{v}|S\rangle = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \langle v\mathbf{k}|\hat{v}|c\mathbf{k}+\mathbf{q}\rangle$$

- Because of non-local pseudopotential and QP corrections, the velocity operator is not the same as the momentum!

$$\hat{v} = i[H,\hat{r}] = \hat{p} + i[V,\hat{r}]$$

use_velocity

- Recommended option!
- Needs WFN_fi and WFNq_fi.
- Specify q-shift: $\mathbf{k}_{\mathrm{WFN}} + \mathbf{q}_{\mathrm{shift}} = \mathbf{k}_{\mathrm{WFNq}}$

$$\langle 0|\hat{v}|S\rangle \approx \frac{\Omega_S}{q} \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \langle v\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|c\mathbf{k}+\mathbf{q}\rangle$$

use_momentum

- Not recommended!
- Needs only WFN.
- Specify polarization $\mathbf{e}_\lambda$ of $\hat{v}$.

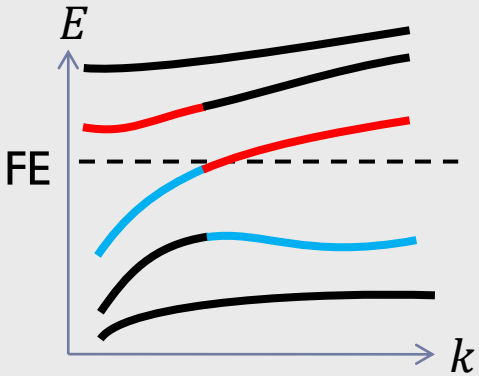
$$\langle v\mathbf{k}|\hat{v}|c\mathbf{k}+\mathbf{q}\rangle \approx \langle v\mathbf{k}|\hat{p}_\lambda|c\mathbf{k}\rangle$$

2. Number of Convergence Knobs

- There are 4 convergence parameters in a typical BSE calculation:
  - # of k-points in the fine grid
  - # of bands in the fine grid
  - # of k-points in the coarse grid
  - # of bands in the coarse grid

Attention!

In kernel/absorption, the number of cond/val bands refer to the number of occ/unocc **states**!



- Uncontrolled approximations:
  - Restricted interpolation (problematic for $\omega \to 0$ in metals)
  - Tamm-Dancoff approximation
  - Static screening

Removed in v. 1.1

3. Quality of the Interpolation

- How to measure the quality of WFN expansion?
- If we include ∞ bands:

$$\sum_{n'} |C^{\mathbf{k}_{\mathrm{co}}}_{n,n'}|^2 = 1$$

- Finite basis set – normalization is reported in files `d?mat_norm.dat`:

```
-------  Norm of dvv matrices : Spins =            1  -------
          k-point           ik_co    v   dist    |dvv|^2
-------------------------------------------------------------
(  0.059 ,  0.046 ,  0.039 )    1    1  0.054   0.987006
(  0.059 ,  0.046 ,  0.039 )    1    2  0.054   0.953488
(  0.059 ,  0.046 ,  0.039 )    1    3  0.054   0.892665
(  0.059 ,  0.046 ,  0.164 )    2    1  0.139   0.923182
```

Before renormalization of coefficients.

- How to get a good interpolation?
  - Include a large number of bands from the coarse grid!
  - Start from a fine enough grid

4. Diagonalization vs. Haydock

- We can get the absorption spectrum $\varepsilon_2(\omega)$ by computing the eigenvalues of $[H]_{\mathrm{fi}}$

- Alternative approach: Haydock iterative scheme
  - Uses the fact that H is Hermitian and computes directly and integrated quantity of H
  - No need to diagonalize matrix!
  - Fast, and scales better with number of processors
  - Drawback: no access to eigenvectors!

absorption.inp with full diagonalization

```
diagonalization

...
```

absorption.inp with Haydock scheme

```
haydock
number_iterations 500
...
```

5. Analyzing Excitons

- Optical spectrum $\varepsilon_2(\omega), \varepsilon_1(\omega)$:
  - absorption_noeh.dat: GW-RPA without local fields
  - absorption_eh.dat: GW-BSE with local fields

- Eigenvalues of the BSE equation Ω_S:
  - eigenvalues.dat: useful to see if there are degeneracies, splitting, etc.

- Where the exciton is coming from:
  - summarize_eigenvectors.x
  - Need to set the flag `write_eigenvalues` in absorption.inp
  - Doesn't work with Haydock!

Wrapping Up

- Interpolation: projection onto bands.
- Why we need 1 coarse WFN and 2 fine WFNs.
- Which k-grid to use for each WFN.

Let's Put the Donkey to Work!

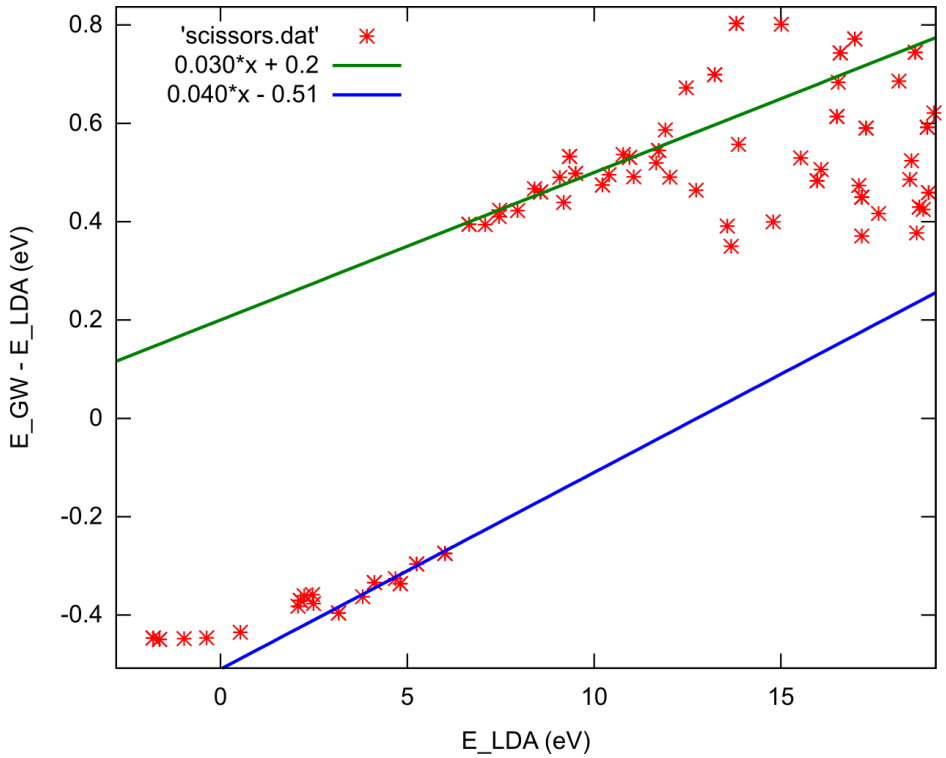
BerkeleyGW

Predicting quasiparticle band structures since 1985.

5. Scissors Operators

- If QP corrections are isotropic and linear with energy, we can approximate the corrections by scissors operators (not recommended)

- Workflow:
  - Calculate Sigma only on a few k-points
  - Plot:
    $\mathrm{E_{cor}} = E_{QP} - E_{LDA}$ v.s E_{LDA}
  - Fit two linear functions: one for conduction and one for valence states



5. Scissors Operators

- What changes:
  - Don't create an eqp_co.dat file
  - Change absorption.inp

absorption.inp with eqp_co.dat

```
...
eqp_co_corrections
...
```

absorption.inp with scissors operators

```
...
evs      <?>
ev0      <?>
evdel    <?>
ecs      <?>
ec0      <?>
ecdel    <?>
...
```

- Where, for $n = \{v, c\}$:

$$E_{QP} = E_{LDA} + Ens + Endel * (E_{LDA} - En0)$$