Practical BSE Calculations with BerkeleyGW + Octopus

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Summary

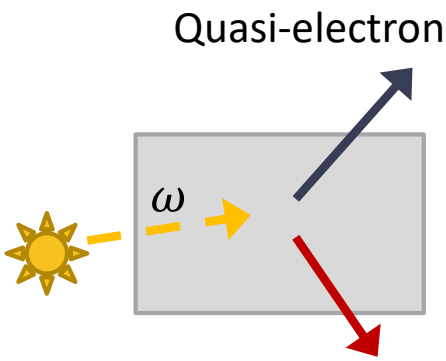
#1 – Theory and Algorithms

#2 – Typical BSE Workflow in BerkeleyGW

#3 – Issues Unique to the BSE Code

Theory Review: Optical Absorption

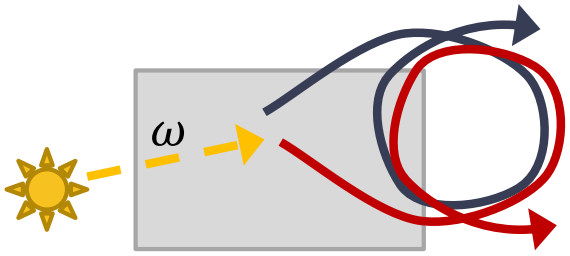
No electron-hole interactions



$$H_{int} \sim \mathbf{A}\cdot\hat{\mathbf{v}}$$

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

With electron-hole interactions



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

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

Solutions of the Bethe-Salpeter equation (BSE)

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

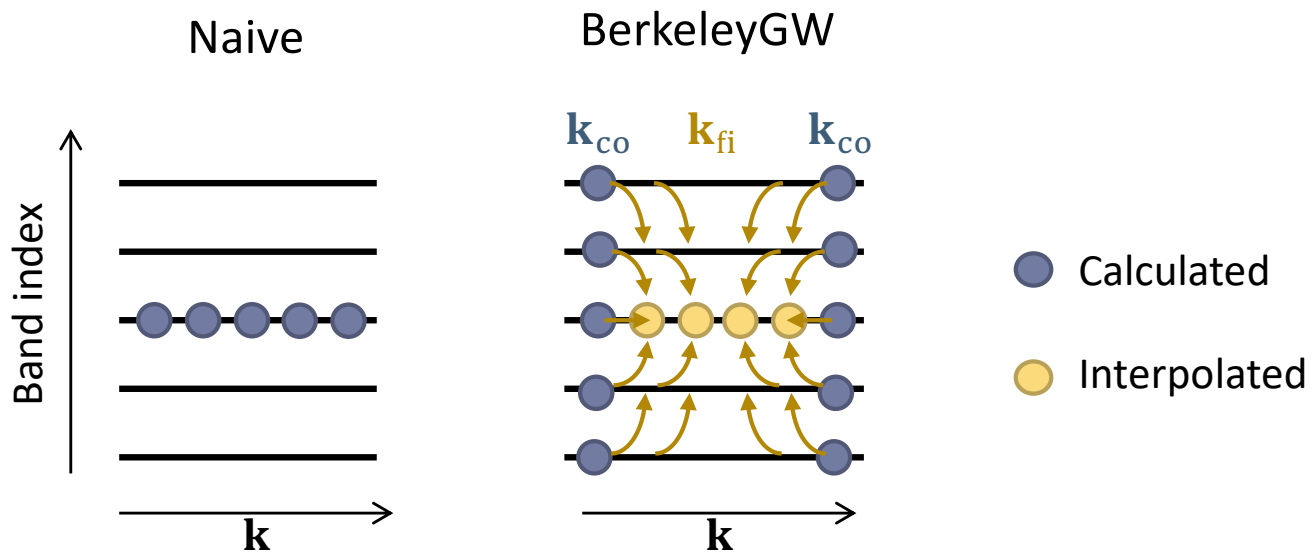
$$u_{n\mathbf{k}_{\mathrm{fi}}} = \sum_{n'} C^{\mathbf{k}_{\mathrm{co}}}_{n,n'} u_{n'\mathbf{k}_{\mathrm{co}}}$$

- 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

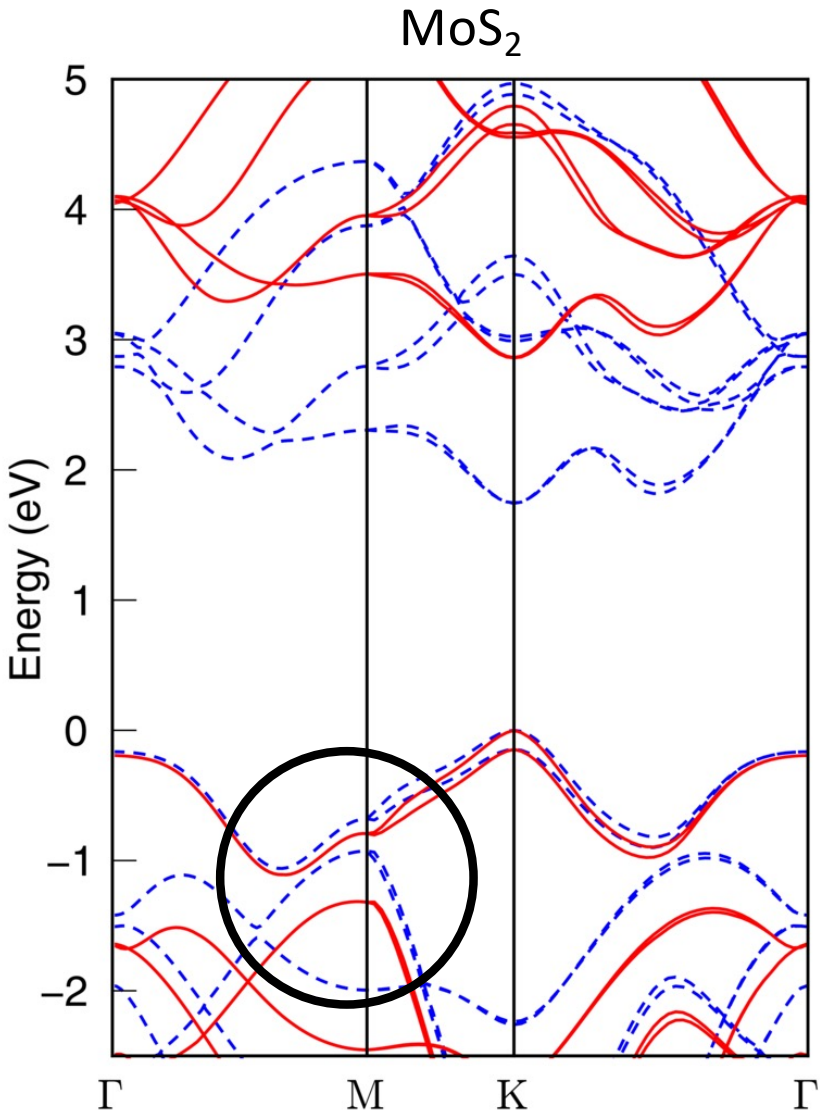
- In practice: trading bands for k-points



- 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!

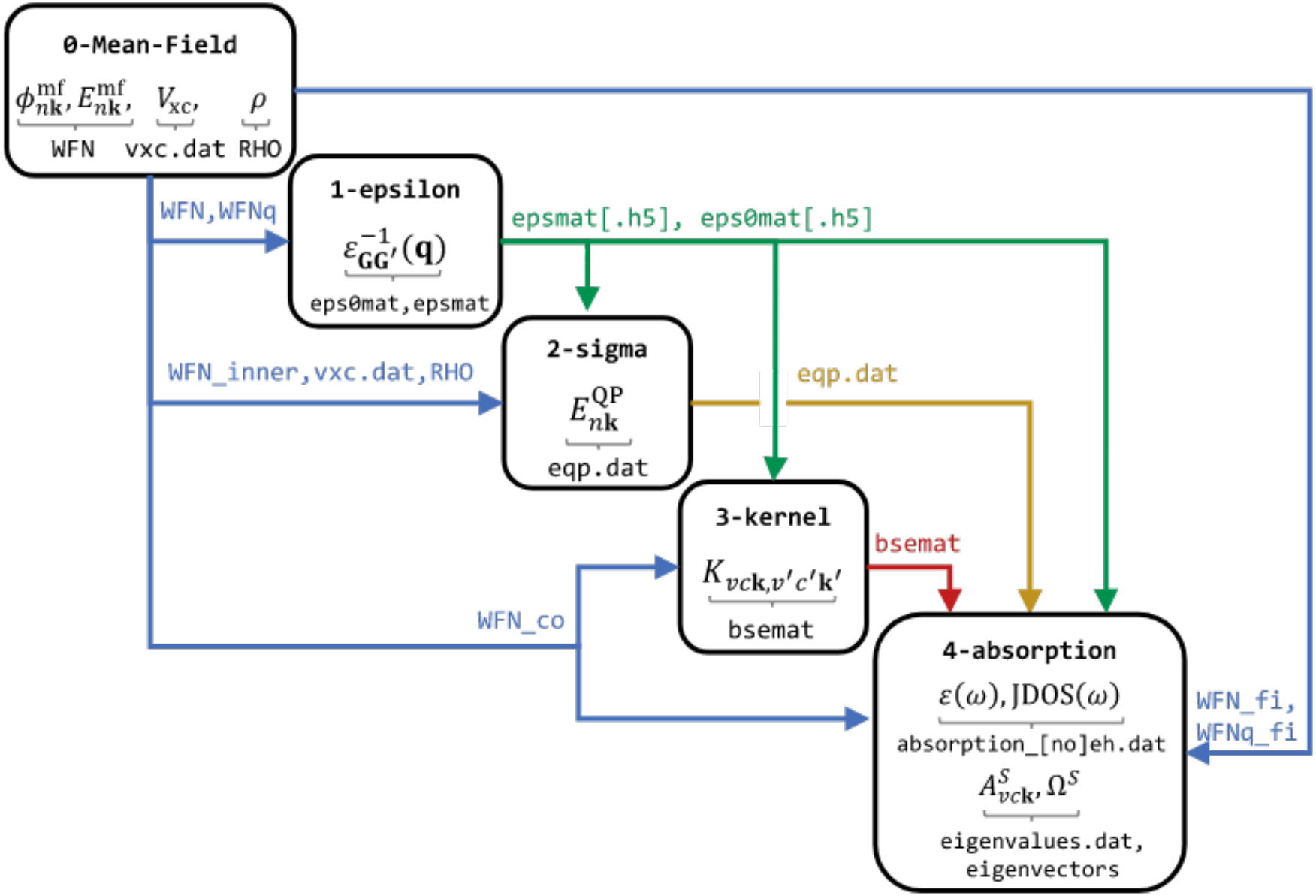


D. Qiu, F. H. da Jornada, S. G. Louie, PRL **111**, 216805 (2013)

Key Points

- Interpolation scheme: trading bands for k-points
- Interpolation of kernel and QP corrections

Typical BSE Workflow in BerkeleyGW



BerkeleyGW Workflow

sigma.x

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

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

kernel.x

Step 2: Calculate BSE kernel on the same coarse grid

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

absorption.x

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

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

… and diagonalize BSE Hamiltonian

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

(Not shown: mean-field, epsilon, convergence)

1. Sigma

sigma.x

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

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

- 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, less reliable (not covered here)

1. Sigma

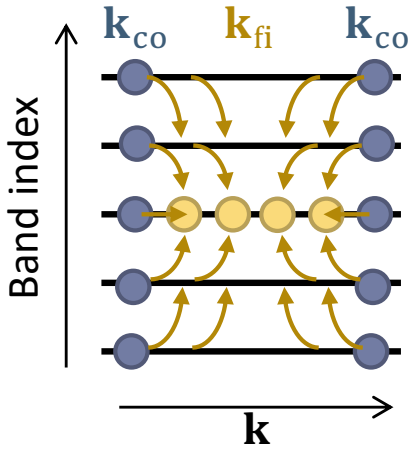
Sample sigma.inp (assuming we are using eqp.dat)

```
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
```

Note the two different # of bands:

$$E_{n\mathbf{k}}^{\mathrm{QP}} \sim \langle n\mathbf{k}|\Sigma|n\mathbf{k}\rangle$$

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



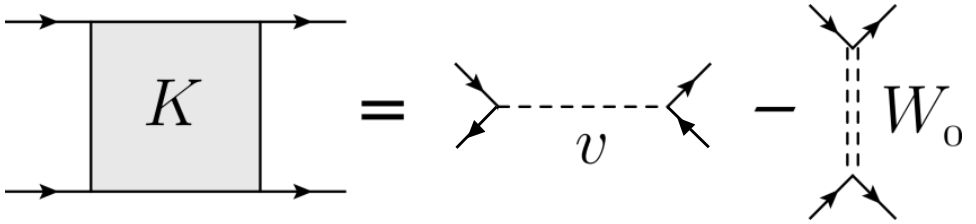
2. Kernel

kernel.x

Step 2: Calculate BSE kernel on the same coarse grid

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

- 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)

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!

Must be ≤ than the # of bands used in Sigma.

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

3. Absorption

absorption.x

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

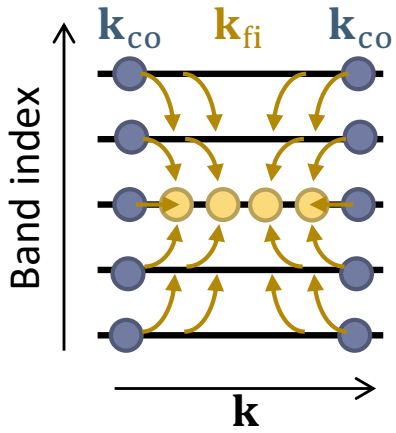
$$[H]_{\mathrm{co}} \Rightarrow [H]_{\mathrm{fi}}$$

… and diagonalize BSE Hamiltonian

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

- Absorption needs same coarse WFN_co from Kernel/Sigma
- Absorption also need two fine WFN files:
  - WFN_fi: for conduction states
  - WFNq_fi: for valence states
- Good practice: use arbitrarily-shifted low-symmetry k-grids
  - This maximizes the number of inequivalent transitions you capture.

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.

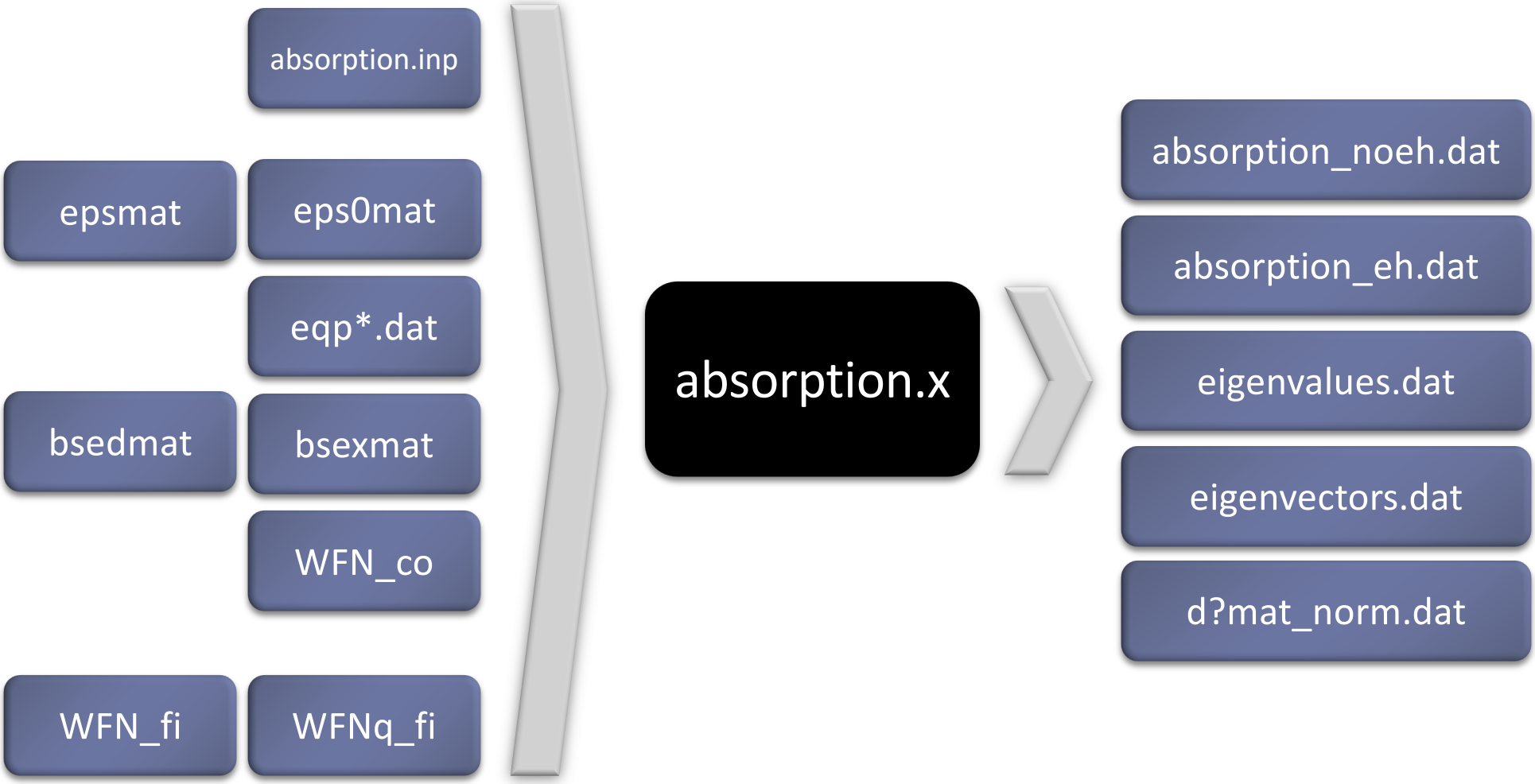
Recommended!

$$\mathbf{k}_{\mathrm{WFN_{fi}}} + \mathbf{q}_{\mathrm{shift}} = \mathbf{k}_{\mathrm{WFNq_{fi}}}$$

Broaden each delta function.

Interpolate eqp_co.dat to eqp.dat

3. Absorption – Workflow



Typical BSE Workflow in BerkeleyGW

Key Points

- BSE codes are separated into two parts:
  - Kernel.x: calculates kernel on coarse grid
  - Absorption.x: interpolates and diagonalizes [H]

- `number_*_bands_coarse`, `number_*_bands_fine`.

Issues Unique to the BSE Code

1. Velocity Operator
2. Finite Systems + Octopus
3. Estimating the Quality of the Interpolation
4. Analyzing Exciton Files
5. Convergence!

1. Velocity Operator

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

- 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: $\mathbf{k}_{\mathrm{WFN_{fi}}} + \mathbf{q}_{\mathrm{shift}} = \mathbf{k}_{\mathrm{WFNq_{fi}}}$

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

use_momentum

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

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

2. Finite Systems + Octopus (benzene)

- For finite systems, Octopus can calculate the single-particle velocity matrix elements directly!
  - No need for two different WFN files and a q-shift in the absorption code.
  - BerkeleyGW can calculate $\varepsilon_2(\mathbf{q} = 0)$ "exactly".

- In BerkeleyGW:

```
...
read_vmtxel
use_momentum
polarization  <...>

skip_interpolation
eqp_corrections
...
```

Read velocity matrix elements from file

Tell BerkeleyGW that there's no q-shift.
Note: this doesn't affect calculation of matrix elements because of the read_vmtxel flag.

There are no k-points, so there's no interpolation! Use directly the eqp.dat file (don't interpolate eqp_co.dat → eqp.dat)

3. Quality of the Interpolation

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

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

- 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. Analyzing Excitons

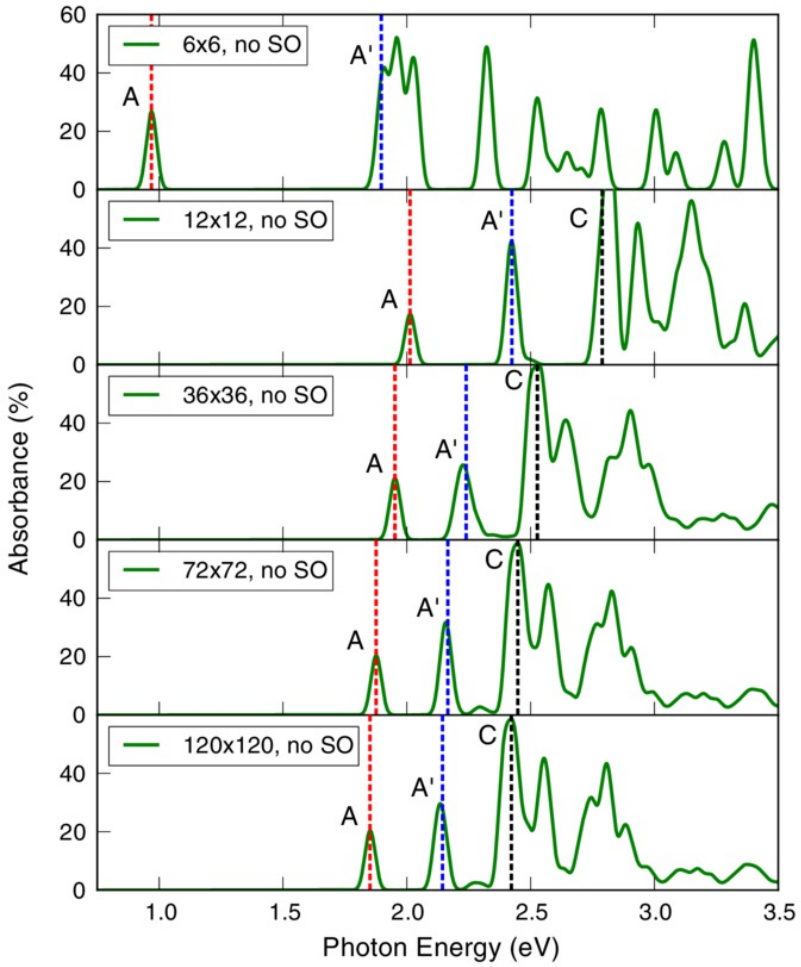
- Optical spectrum $\varepsilon_2(\omega), \varepsilon_1(\omega)$:
  - absorption_noeh.dat: GW-RPA without local fields
  - absorption_eh.dat: GW-BSE with local fields

- Eigenvalues of the BSE equation Ω_S:
  - eigenvalues.dat: useful to see if there are degeneracies, splitting, etc. or whether there are "dark" states not contributing the optical spectrum

- Where the exciton is coming from:
  - summarize_eigenvectors.x
  - Need to set the flag `write_eigenvalues` in absorption.inp

5. Convergence!

- 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



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A paper about converging properly, with an erratum about further convergence…

Make sure you converge your calculations!

Issues Unique to the BSE Code

1. Velocity operator

Key Points

- Why we need 2 WFN files: velocity operator
- **Convergence!**

5. Convergence!