Practical BSE Calculations with BerkeleyGW

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(Adapted from presentation by Felipe Jornada)

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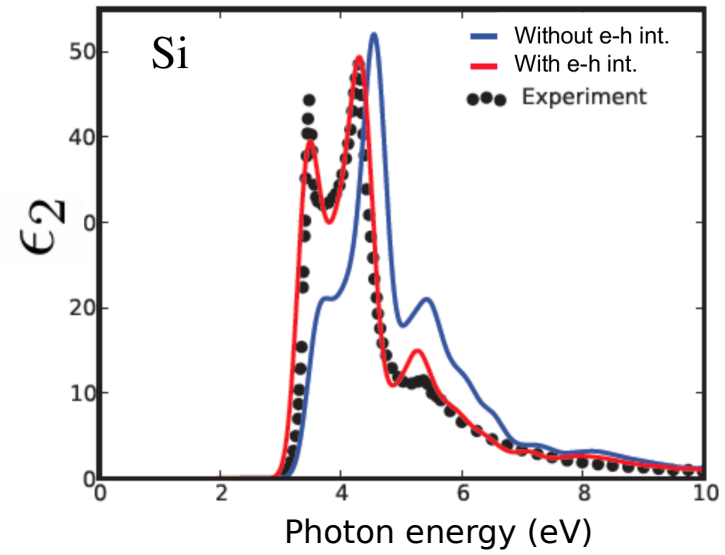
Yale

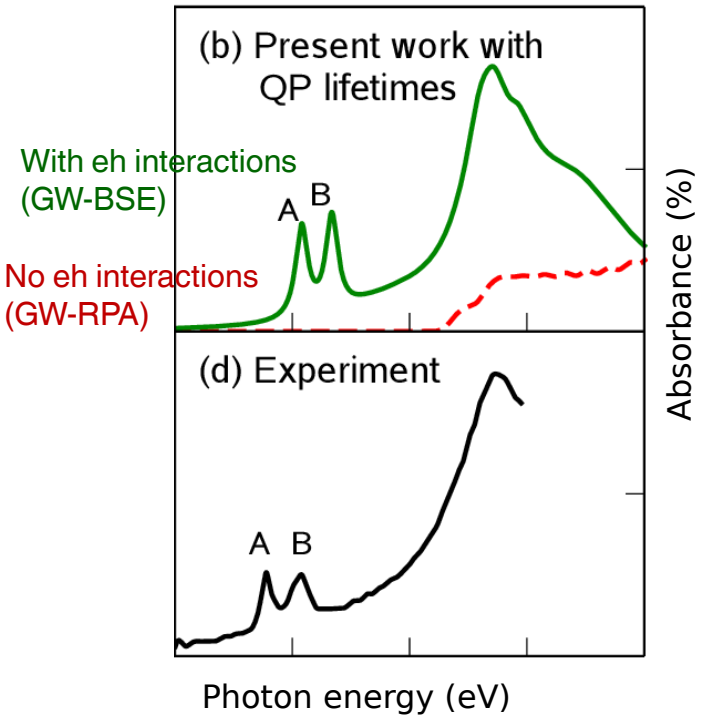
C2SEPEM

Optical Absorption Spectrum

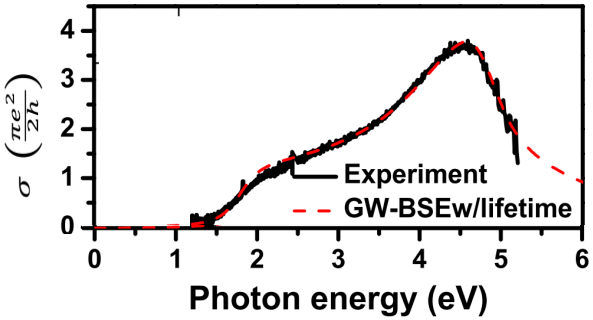
Silicon [1]



MoS_2 [2]



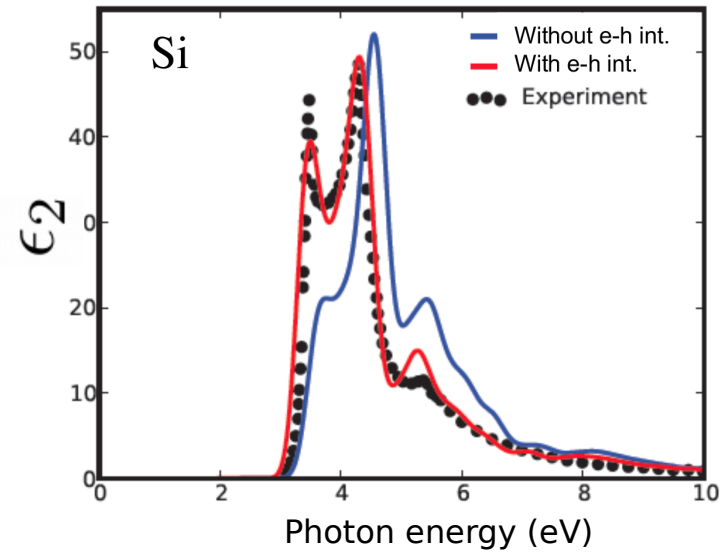
Doped Graphene [3]



[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] K. F. Mak, F. H. da Jornada, et al., PRL 112, 207401 (2014).

Optical Absorption Spectrum

Silicon [1]



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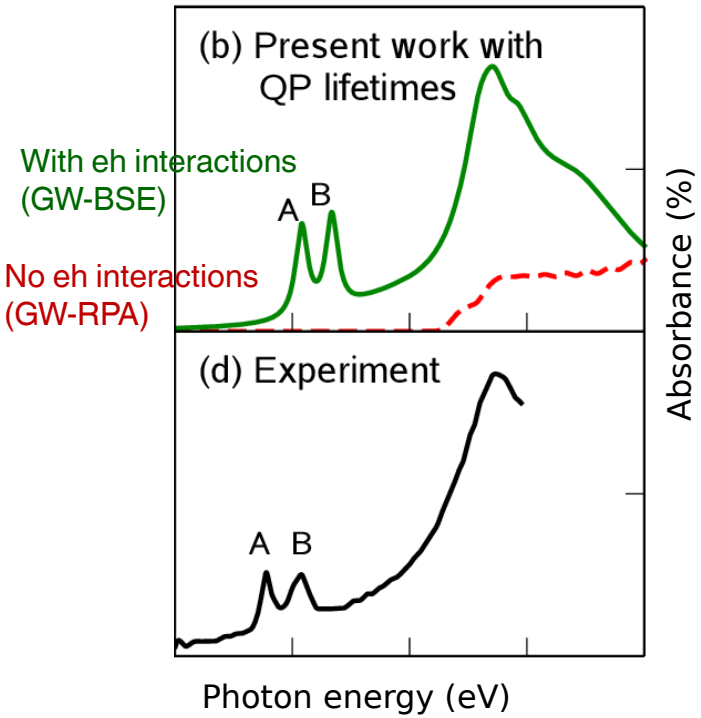

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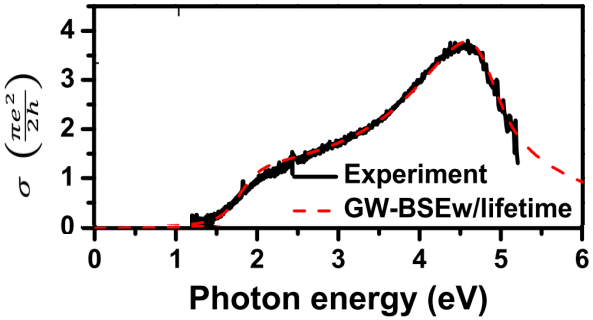

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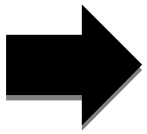
Outline

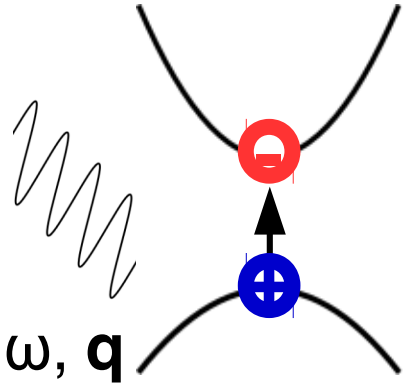


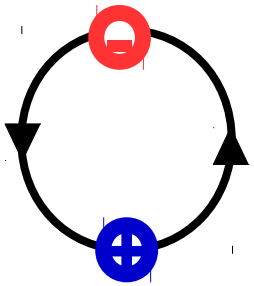
#1 – Theoretical and methodological overview

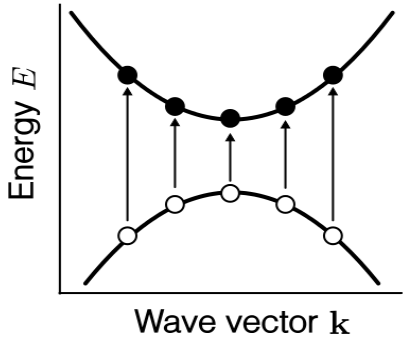
#2 – Typical BSE workflow in BerkeleyGW

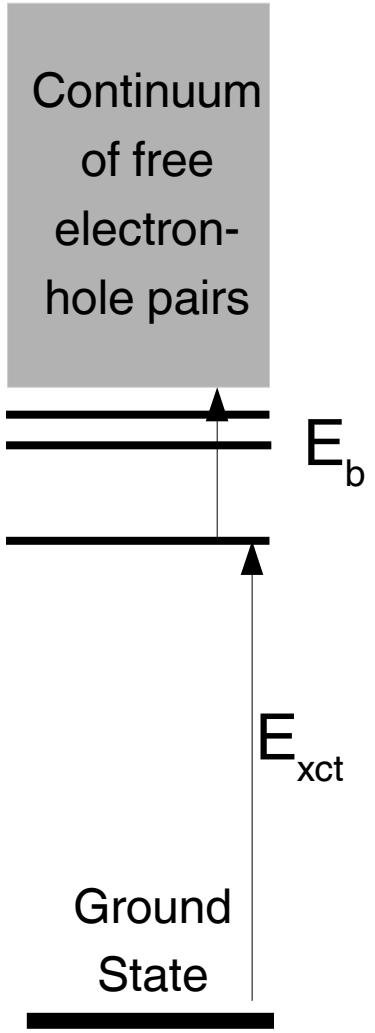
#3 – Issues unique to the BSE code

Theory Overview – Excitons









Incoming photon excites quasi-electron and quasi-hole

Electron and hole interact forming an **exciton**

Exciton State:

$$\Psi_S(\mathbf{r}_e, \mathbf{r}_h)$$

$$= \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \psi^*_{v\mathbf{k}}(\mathbf{r}_h) \psi_{c\mathbf{k}}(\mathbf{r}_e)$$

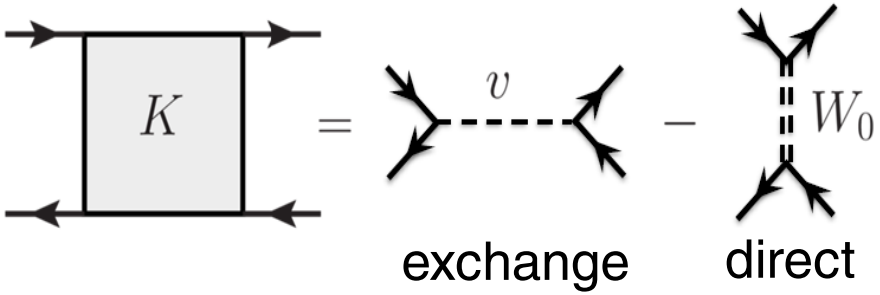
Theory Overview: GW-BSE

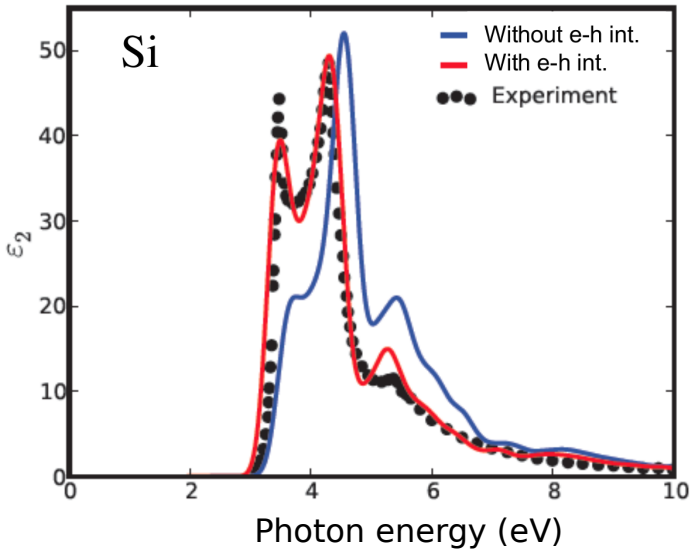
- Bethe-Salpeter Equation → Effective Hamiltonian:

$$H^{\mathrm{BSE}}\Psi_S(\mathbf{r}_e,\mathbf{r}_h) = \Omega_S\Psi_S(\mathbf{r}_e,\mathbf{r}_h)$$

$$H^{\mathrm{BSE}}_{vc\mathbf{k},v'c'\mathbf{k}'} = (E_{c\mathbf{k}} - E_{v\mathbf{k}})\delta_{\mathbf{k},\mathbf{k}'} + K_{vc\mathbf{k},v'c'\mathbf{k}'}$$

- Interaction Kernel





- Absorption

$$\epsilon_2 \propto \sum_S |\langle 0|\mathbf{v}|S\rangle|^2 \delta(\omega - \Omega_S)$$

Rohlfing and Louie, *PRB* 62, 4947 (2000). Deslippe et al, *Comput. Phys. Commun.* 183, 1269 (2012).

Methodological Overview: BerkeleyGW Interpolation Scheme

Challenge: compute quasiparticle corrections and kernel matrix elements on a VERY FINE K-GRID!

Eg: 300x300 k-grid for MoS_2

Methodological Overview: BerkeleyGW Interpolation Scheme

- Expensive to compute kernel matrix elements $\langle vc\mathbf{k}_{fi}|K|v'c'\mathbf{k}'_{fi}\rangle$
- Strategy: $\langle vc\mathbf{k}_{co}|K|v'c'\mathbf{k}'_{co}\rangle \longrightarrow \langle vc\mathbf{k}_{fi}|K|v'c'\mathbf{k}'_{fi}\rangle$

- BerkeleyGW: projection interpolation
  - Explicitly generate coarse- and fine-grid WFNs
  - Expand fine-grid WFNs in term of coarse-grid WFNs.
  - No need to perform Wannier interpolation, etc.
  - Captures band crossing, etc.

Methodological Overview: BerkeleyGW Interpolation Scheme

- Step 0: Obtain WFNs on a coarse and fine grid.
- Step 1: Expand fine WFNs in terms of coarse WFNs

$$u_{n\mathbf{k}_{\text{fi}}} = \sum_{n'} C^{\mathbf{k}_{\text{co}}}_{n,n'} u_{n'\mathbf{k}_{\text{co}}} \qquad C^{\mathbf{k}_{\text{co}}}_{n,n'} = \int d\mathbf{r}\, u_{n\mathbf{k}_{\text{fi}}}(\mathbf{r}) u^*_{n'\mathbf{k}_{\text{co}}}(\mathbf{r})$$

- Step 2: Interpolate QP energies (assume Σ is diagonal in $(n\mathbf{k})$):

$$E^{\text{QP}}_n(\mathbf{k}_{\text{fi}}) = \quad E^{\text{MF}}_n(\mathbf{k}_{\text{fi}}) + \left\langle \sum_{n'} \left| C^{\mathbf{k}_{\text{co}}}_{n,n'} \right|^2 \left(E^{\text{QP}}_{n'}(\mathbf{k}_{\text{co}}) - E^{\text{MF}}_{n'}(\mathbf{k}_{\text{co}}) \right) \right\rangle_{\mathbf{k}_{\text{co}}}$$

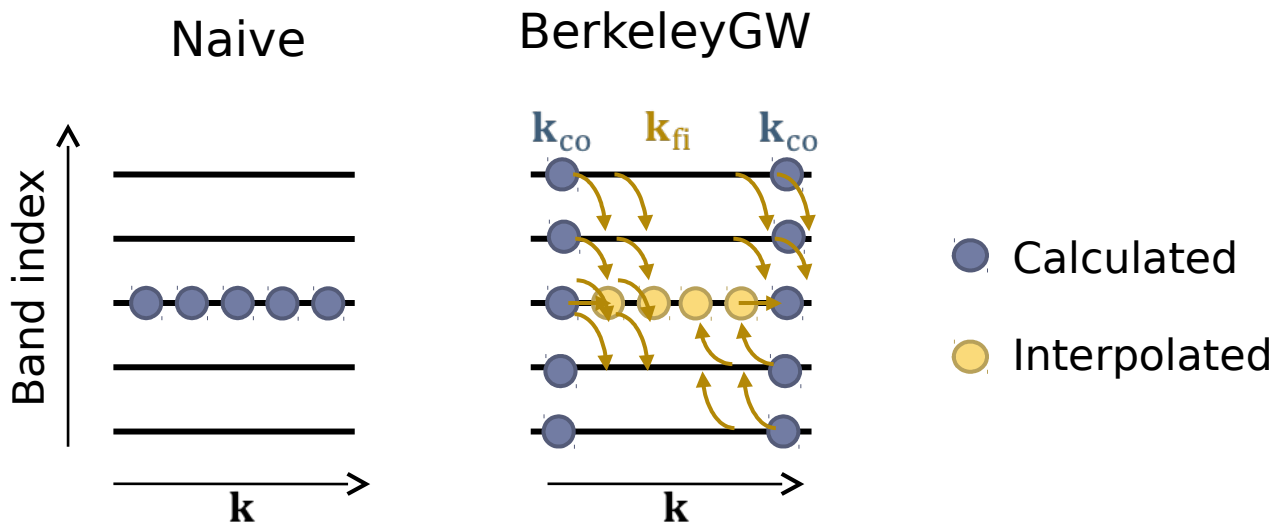
- Step 3: Interpolate BSE kernel matrix elements (head+wings+body)

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

BERKELEYGW INTERPOLATION SCHEME

- In practice: trading bands for k-points

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

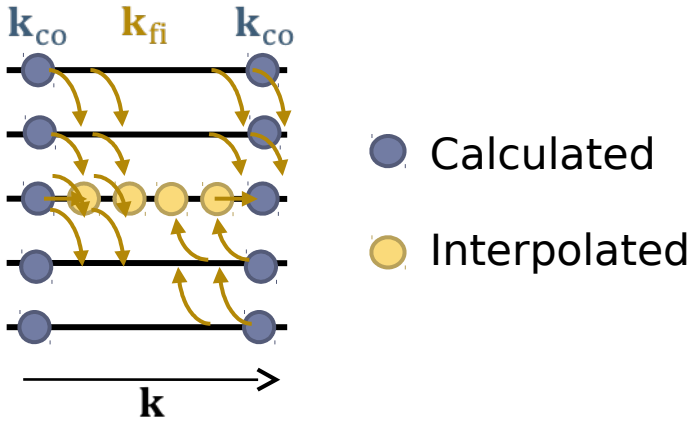


- How to get a good interpolation?
  - Include a large number of bands from the coarse grid and start from a coarse grid that is not too coarse.

BERKELEYGW INTERPOLATION SCHEME

- Did I include enough bands?

$$\mathrm{Error}(\mathrm{n}, \mathbf{k}_{\mathrm{fi}}) = 1 - \sum_{n'} \left| C_{n,n'}^{\mathbf{k}_{\mathrm{fi}}} \right|^2$$

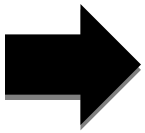


- Detail of “completion relation”:
  - **`dvmat_norm.dat`**
  - **`dcmat_norm.dat`**

- **`absorption.out / inteqp.out`**

Outline

#1 – Theoretical and methodological overview



#2 – Typical BSE workflow in BerkeleyGW

#3 – Issues unique to the BSE code

BERKELEYGW WORKFLOW

Step 0: Calculate QP–corrected band structure on a coarse grid

`epsmat.h5`, $\{E_c\}_{\text{co}}$, $\{E_v\}_{\text{co}}$

`kernel.x`

Step 1: Calculate BSE kernel on the same coarse grid

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

`absorption.x`

Step 2: Interpolate to a fine k-grid and build BSE Hamiltonian…

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

… and diagonalize BSE Hamiltonian

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

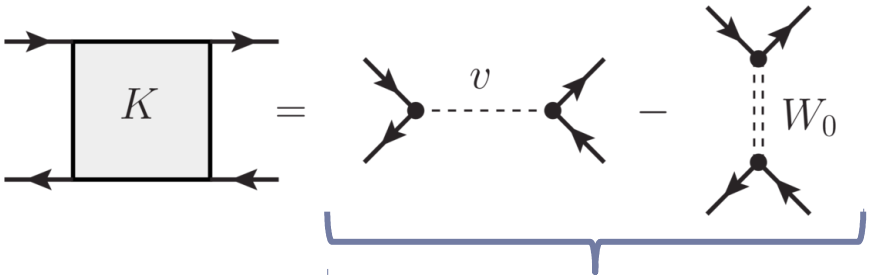
1. KERNEL

kernel.x

Step 1: Calculate BSE kernel on the same coarse grid

$$[K]_{co}$$

- Time consuming: Computes $(n_v n_c n_k)^2$ matrix elements
- Uses a coarse-grid WFN_co



bsemat.h5

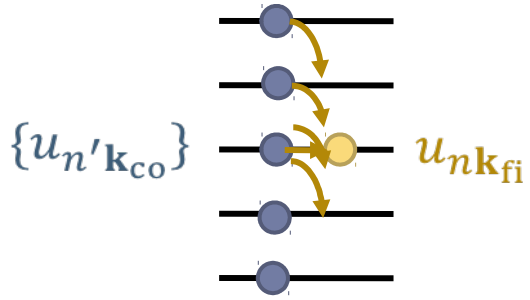
- Recommended:
  - Use same WFN_co as in Sigma (WFN_inner)

1. KERNEL

Sample **`kernel.inp`**

```
number_val_bands <?>
number_cond_bands <?>

<?>_symmetries_coarse_grid
screening_<?>
```



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

Bands counted wrt FE:

- vbm, vbm-1, …
- cbm, cbm+1, …

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

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

2. ABSORPTION

absorption.x

Step 2: 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

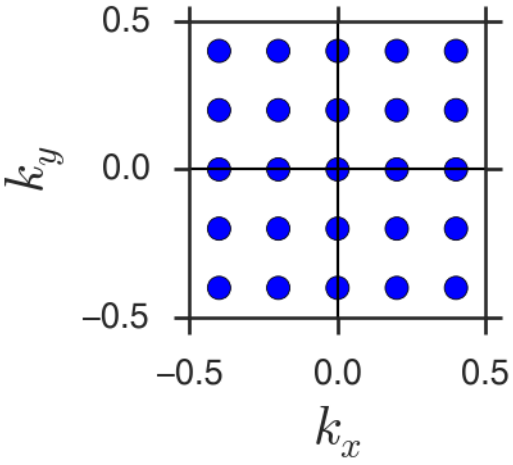
$$\varepsilon_2(-\mathbf{q},\omega) \propto \sum_S |\langle 0|\hat{v}|S\rangle|^2 \delta[\omega - \Omega_S] \qquad \langle 0|\hat{v}|S\rangle = \frac{\Omega_S}{q}\sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \langle v\mathbf{k}+\mathbf{q}|e^{-i\mathbf{q}\cdot\mathbf{r}}|c\mathbf{k}\rangle$$

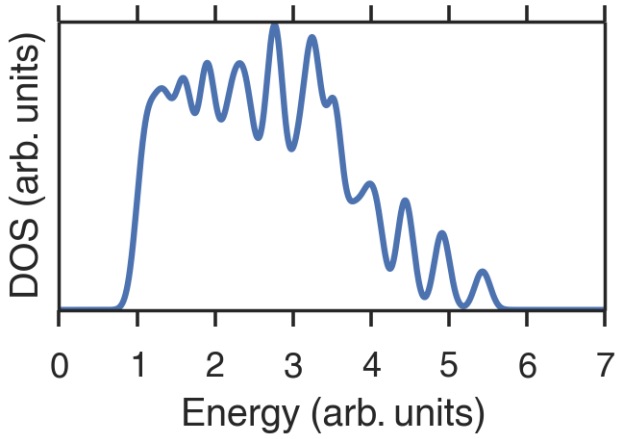
- Typically q is 10^{-3}
- We need two fine WFN files:
  - WFN_fi: for conduction states $|c\mathbf{k}\rangle$
  - WFNq_fi: for q-shifted valence states $|v\mathbf{k}+\mathbf{q}\rangle$

Direction of **q** = polarization of light= difference WFNq and in WFN

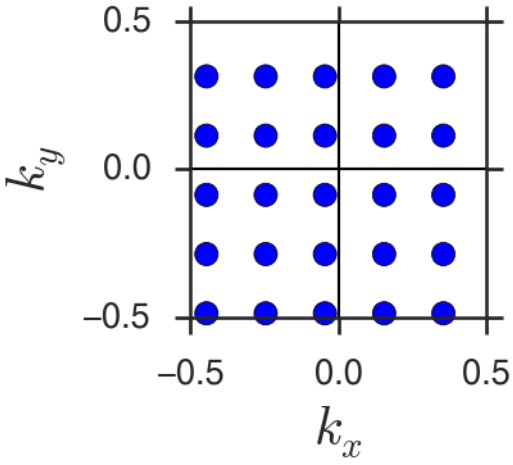
2. ABSORPTION – RANDOMLY SHIFTED K-GRIDS

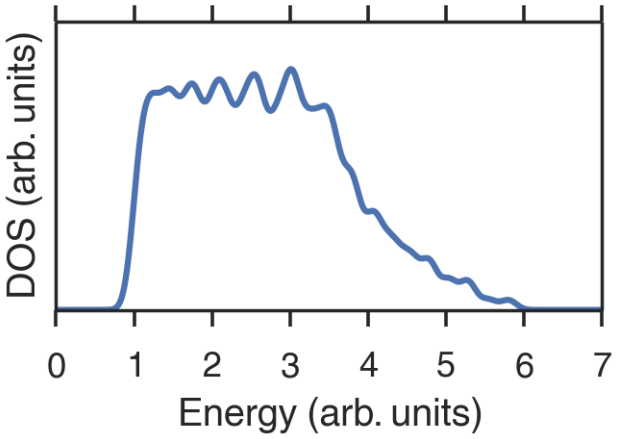
WFN_fi, no k-shift



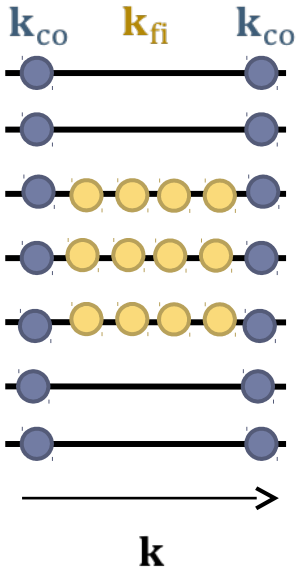


WFN_fi, random k-shift





2. ABSORPTION



Sample **`absorption.inp`**

```
diagonalization

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

use_symmetries_coarse_grid
no_symmetries_fine_grid
no_symmetries_shifted_grid

screening_semiconductor

use_velocity

gaussian_broadening
energy_resolution 0.15

eqp_co_corrections
```

Unshifted grid (WFN_co)

Both randomly shifted grids (WFN_fi and WFNq_fi)

Broaden each delta function.

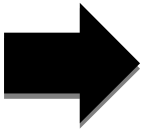
Interpolate `eqp_co.dat`

OUTLINE

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. Convergence
2. Analyzing results
3. Other features

1. 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

- Some rules of thumb:
  - # of bands in fine grid: energy window + binding energy (~ EASY)
  - # of bands in the coarse grid: estimate from **`inteqp.x`**
  - # of k-points in coarse grid ~ **`sigma.x`** (FOR BULK SYSTEMS ONLY)

2. ANALYZING EXCITONS

- Optical spectrum : $\epsilon_2(\omega),\ \epsilon_1(\omega)$
  - **absorption_noeh.dat**: GW-RPA
  - **absorption_eh.dat**: GW-BSE

- Eigenvalues of the BSE equation :
  - **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_eigenvectors** in **absorption.inp**

3. OTHER FEATURES

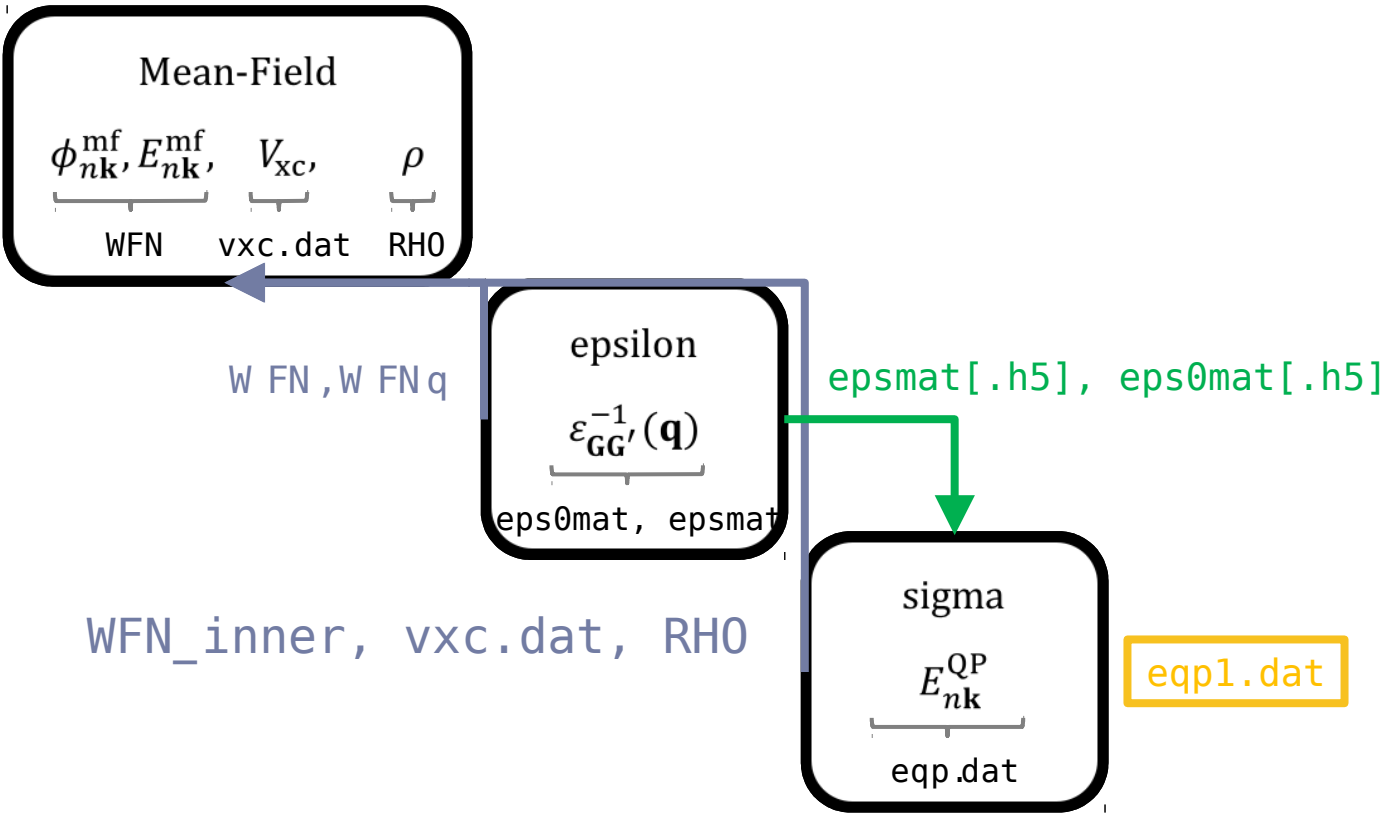
- Some other features:
  - Haydock/Lanczos methods: iterative solution for the absorption spectrum. No evecs can be obtained.
  - Unrestricted interpolation: improves the quality of the interpolation by allowing mixtures of conduction and valence states. Important for metals!
  - Momentum operator: allows you not to use WFNq_fi file (but neglects non-local part of PP and)

- Approximations:
  - Tamm-Dancoff approximation (optional)
  - Static screening

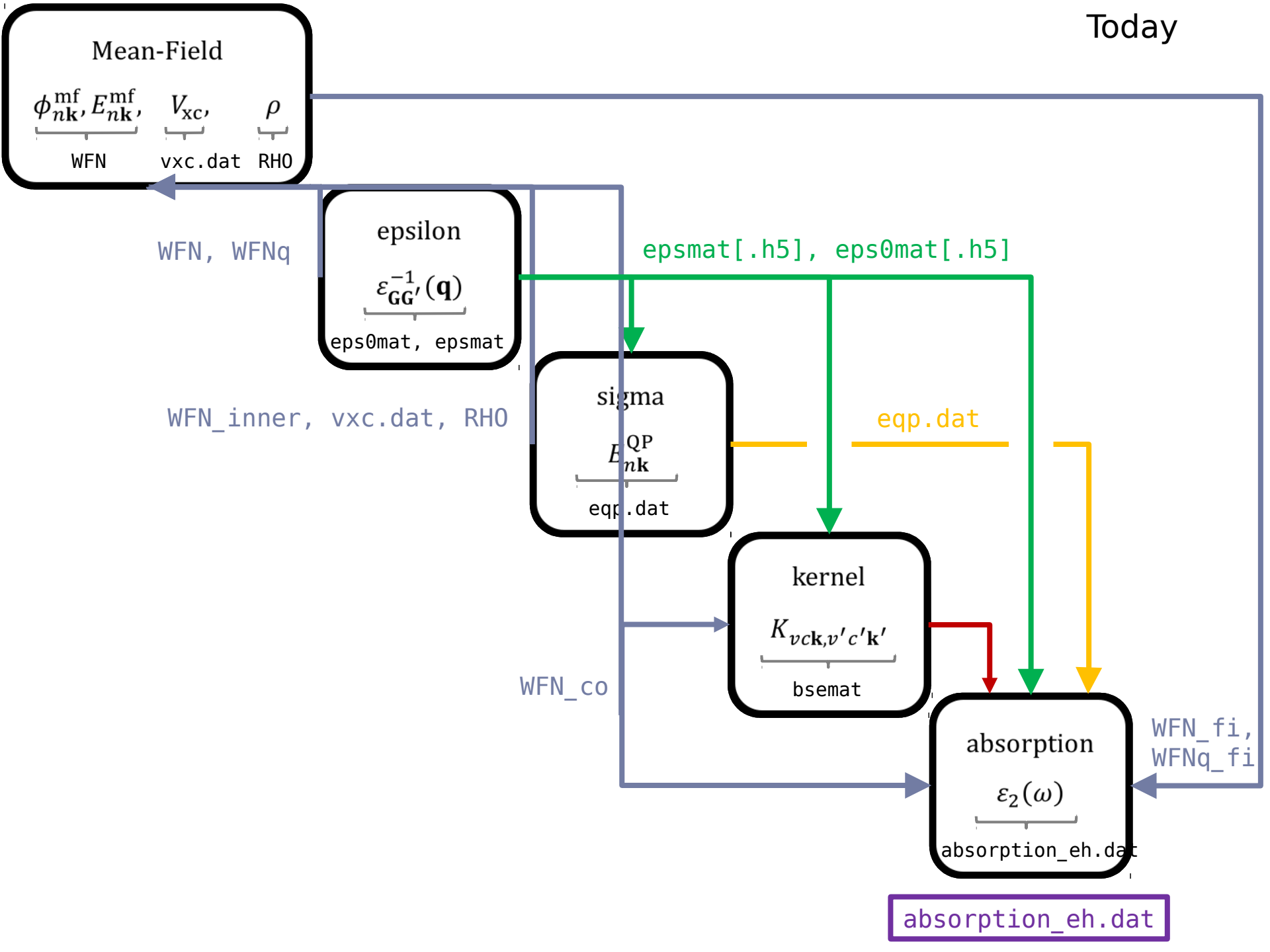
SUMMARY

- BSE needs to be solved on fine k-grid
- BGW interp.: projection of fine WFNs onto coarse WFNs
  - Need to *include more bands* in kernel calculation
- WFNs:
  - Kernel: WFN_co
  - Absorption: WFN_co, WFN_fi, WFNq_fi
  - WFN_co: unshifted
  - WFN_fi: random k-shift
  - WFNq_fi: random k-shift + q-shift (dir. = pol. of light)
- 4 convergence parameters: {bands, **kpts**} x {co, **fi**}

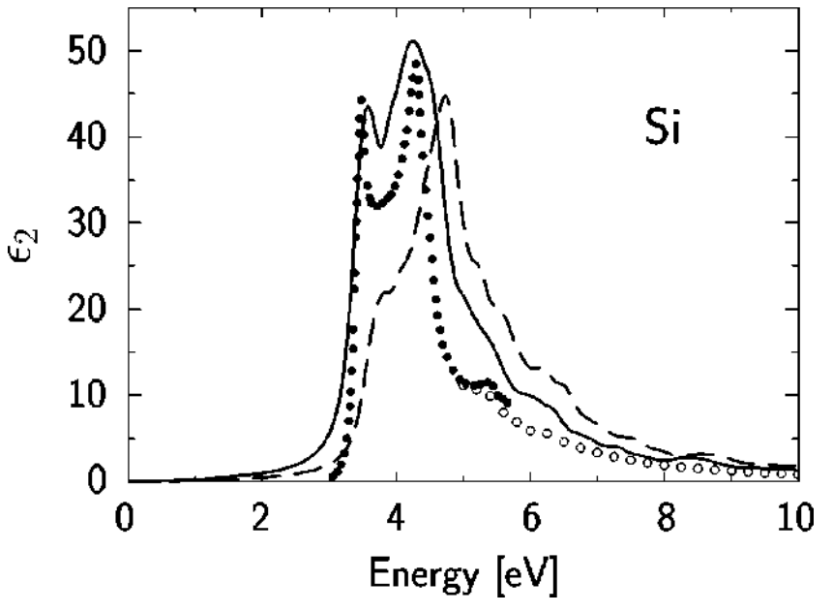
Yesterday


Mean-Field
$\phi^{mf}_{n\mathbf{k}}, E^{mf}_{n\mathbf{k}}$, V_{xc}, ρ
WFN
vxc.dat
RHO
WFN, WFNq
epsilon
$\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q})$
eps0mat, epsmat
epsmat[.h5], eps0mat[.h5]
WFN_inner, vxc.dat, RHO
sigma
$E^{QP}_{n\mathbf{k}}$
eqp.dat
eqp1.dat

Today


Mean-Field
$\phi^{mf}_{n\mathbf{k}}, E^{mf}_{n\mathbf{k}}$, V_{xc}, ρ
WFN
vxc.dat
RHO
WFN, WFNq
epsilon
$\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q})$
eps0mat, epsmat
epsmat[.h5], eps0mat[.h5]
WFN_inner, vxc.dat, RHO
sigma
$E^{QP}_{n\mathbf{k}}$
eqp.dat
eqp.dat
kernel
$K_{vc\mathbf{k},v'c'\mathbf{k}'}$
bsemat
WFN_co
absorption
$\varepsilon_2(\omega)$
absorption_eh.dat
WFN_fi,
WFNq_fi
absorption_eh.dat

HANDS-ON SESSION 2 – ABSORPTION SPECTRUM OF SILICON



- Goals:
  - Reproduce plots on the left
  - Partial convergence study wrt k-point sampling and number of bands

M. Rohlfing, S. G. Louie, PRB **62**, 8 (2000).

EXTRA SLIDES

BERKELEYGW INTERPOLATION SCHEME

- **`inteqp.out`** from yesterday's session:

```
 Max. error in norm of transformation coefficients (1 - \sum_co |d_fi,co|
^2):
- For valence states: 2.887E-01
- For conduction states: 1.000E+00

WARNING: there are fine/coarse transformation coefficients with 2-norm <
95%.
To improve convergence, you might want to consider:
- using the "unrestricted_transformation" flag in the input file
- including more bands from the coarse WFN_co file
(number_*_bands_coarse)
- using a coarse WFN_co file with a denser k-mesh
```

- Error = 100% for conduction states?!
- Where is it coming from?

BERKELEYGW INTERPOLATION SCHEME

- dcmat_norm.dat from yesterday's session:

```
 -------  Norm of dcc matrices : Spins =           1  -------
          k-point           ik_co    c   dist    |dcc|^2
-------------------------------------------------------------------
 (  0.500 ,  0.500 ,  0.500 )   13    1  0.000   1.000000
[...]
 (  0.367 ,  0.000 ,  0.367 )   18    9  0.144   0.878516
 (  0.367 ,  0.000 ,  0.367 )   18   10  0.144   0.000000
 (  0.378 ,  0.000 ,  0.378 )   58    1  0.150   0.988656
```

- Band crossing. Look at **`inteqp.inp`**:

```
number_val_bands_coarse 4
number_val_bands_fine 4
number_cond_bands_coarse 10
number_cond_bands_fine 10
```

- #fi bands = # co bands! This is a bad idea is general!!
- But we didn't plot the 10th cond. band, so it's alright ⏪