Tutorial: Octopus + BerkeleyGW

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BerkeleyGW

octopus

NERSC

Benasque
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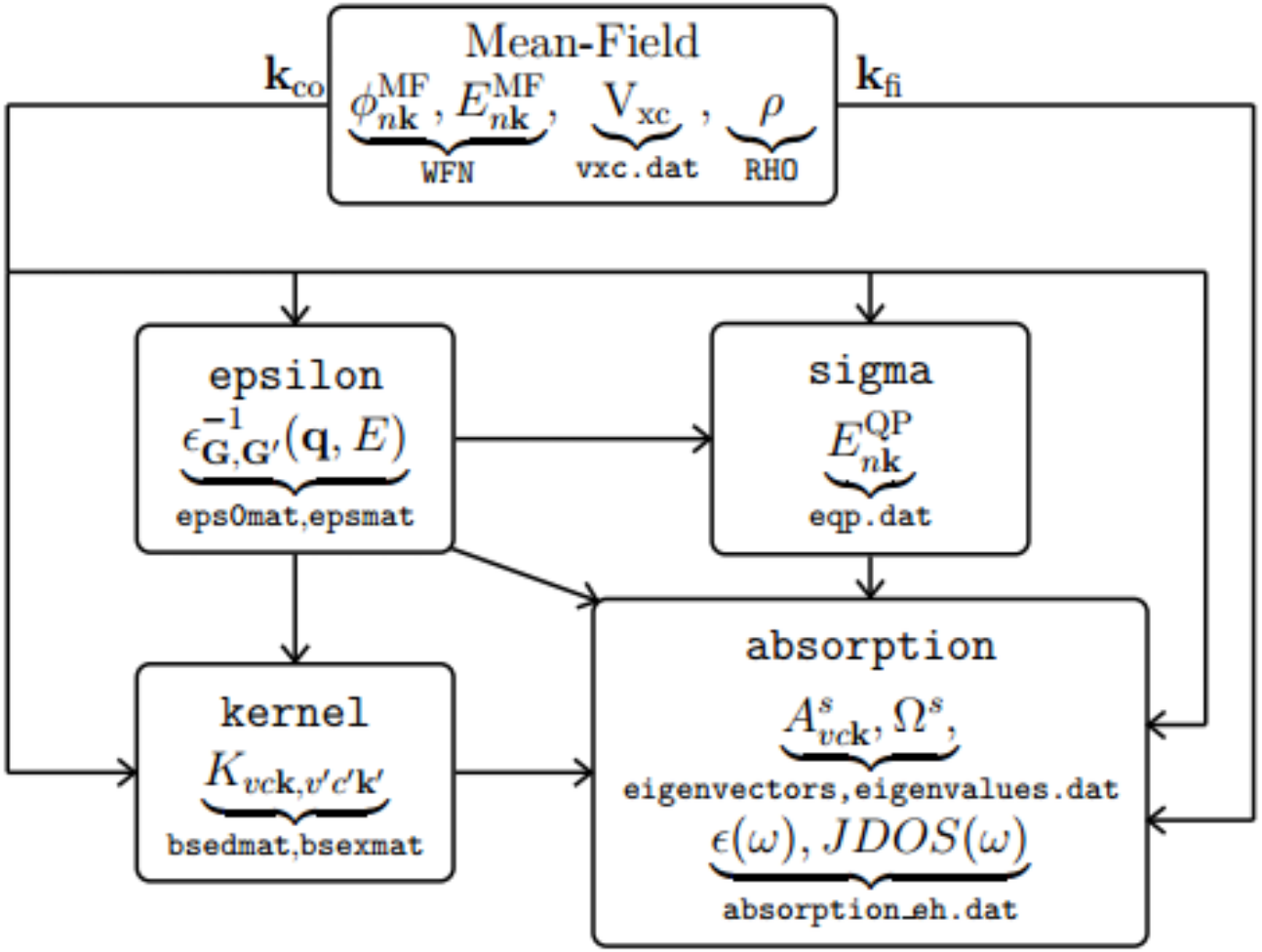
Why Use BerkeleyGW

- Supports a large set of Mean-Field codes: PARATEC, Quantum ESPRESSO, Octopus, PARSEC, SIESTA, EPM (TBPW)
- Supports 3D, 2D, 1D and Molecular Systems. Coulomb Truncation
- Support for Semiconductor, Metallic and Semi-Metallic Systems
- Efficient Algorithms and Use of Libraries. (BLAS, FFTW, LAPACK, SCALAPACK, FFTW) (OpenMP, FFTW3, HDF5 in BGW 1.1)
- Massively Parallel. Scales to 100,000 CPUs, distributed Memory.
- Efficient accurate solution to BSE via k-point Interpolation
- Support for LDA/GGA/Hybrid/HF/COHSEX starting points as well as off-diagonal Σ calculations

GW Method


Mean-Field
$\mathbf{k}_{\mathrm{co}}$
$\mathbf{k}_{\mathrm{fi}}$
$\phi^{\mathrm{MF}}_{n\mathbf{k}}, E^{\mathrm{MF}}_{n\mathbf{k}}$
WFN
V_{xc}
vxc.dat
ρ
RHO
epsilon
$\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, E)$
eps0mat,epsmat
sigma
$E^{\mathrm{QP}}_{n\mathbf{k}}$
eqp.dat
kernel
$K_{vc\mathbf{k},v'c'\mathbf{k}'}$
bsedmat,bsexmat
absorption
$A^s_{vc\mathbf{k}}, \Omega^s,$
eigenvectors,eigenvalues.dat
$\epsilon(\omega), JDOS(\omega)$
absorption_eh.dat

Full-Frequency vs. GPP

-The relative accuracy of Full-Frequency vs. Generalized Plasmon Pole (GPP) calculations is somewhat contentious.

$$\langle n\mathbf{k}|\,\Sigma_{\mathrm{CH}}(E)\,|n'\mathbf{k}\rangle = \frac{i}{2\pi}\sum_{n''}\sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} M^{*}_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G})M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}') \quad (20)$$
$$\times \int_0^\infty dE' \, \frac{\left[\epsilon^{\mathrm{r}}_{\mathbf{G}\mathbf{G}'}\right]^{-1}(\mathbf{q};E') - \left[\epsilon^{\mathrm{a}}_{\mathbf{G}\mathbf{G}'}\right]^{-1}(\mathbf{q};E')}{E - E_{n''\mathbf{k}-\mathbf{q}} - E' + i\delta} \; v(\mathbf{q}+\mathbf{G}')$$

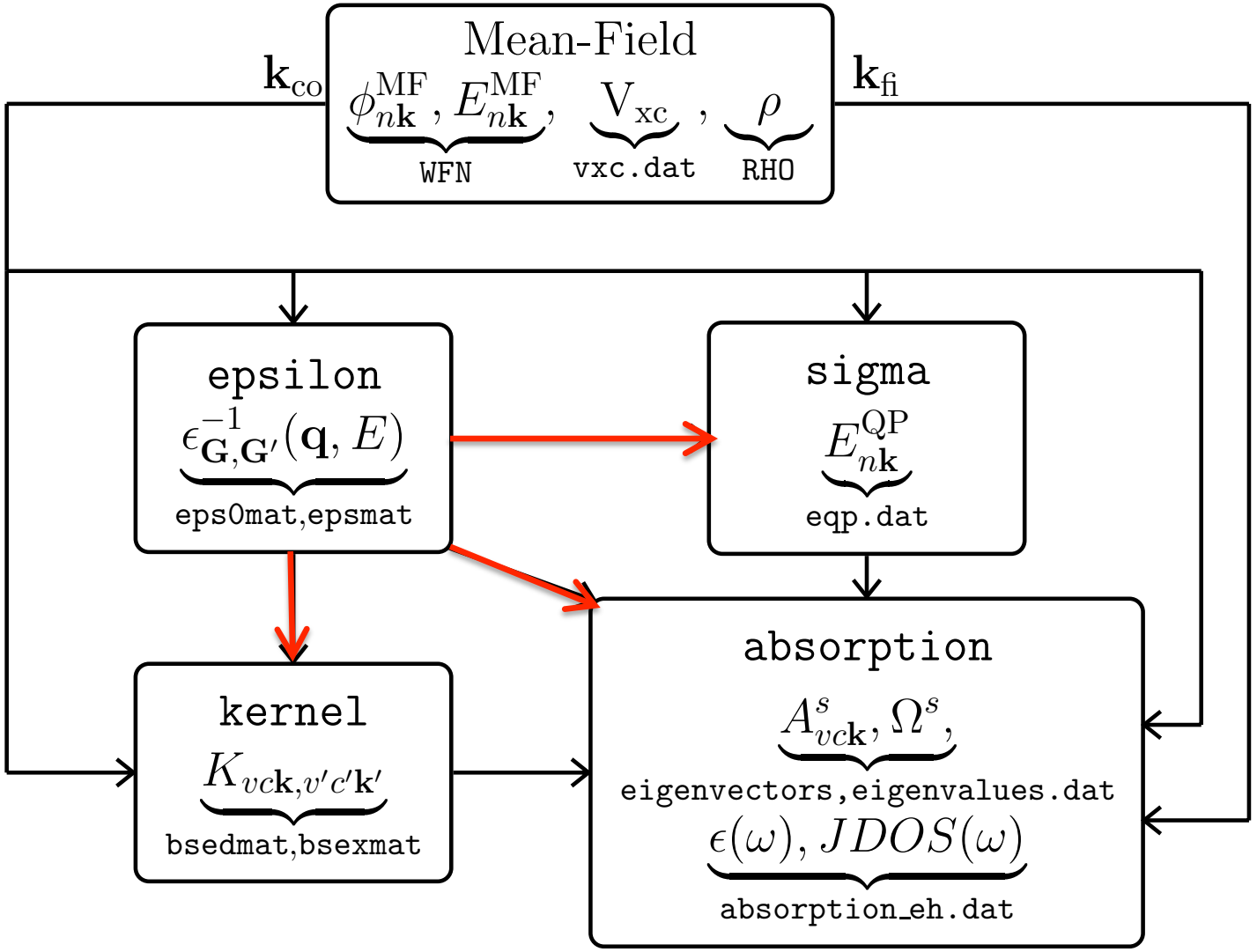
GPP is significantly faster, the integral over frequencies can be performed analytically if assume the dielectric response is dominated by a single plasmon pole.

BerkeleyGW supports both. With full-frequency you can compute spectral functions, lifetimes and weights.

Practical issues

1. Screening models for Epsilon
2. Construction of **k**-grids
3. Symmetry and degeneracy
4. Real and complex version
5. Convergence

Screening models: How do we use ε?



Screening models: How do we use ε?

Sigma integrates over **q** with $\varepsilon^{-1}(\mathbf{q})$

$$\langle n\mathbf{k}|\,\Sigma(E)\,|n'\mathbf{k}\rangle = \frac{i}{2\pi}\sum_{n''}\sum_{\mathbf{qGG'}} M^*_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G})M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G'})$$
$$\times\int_{-\infty}^{\infty} dE' e^{-i\delta E'}\frac{\left[\epsilon_{\mathbf{GG'}}\right]^{-1}(\mathbf{q};E')}{E-E_{n''\mathbf{k}-\mathbf{q}}-E'-i\delta_{n''\mathbf{k}-\mathbf{q}}}v(\mathbf{q}+\mathbf{G'})$$

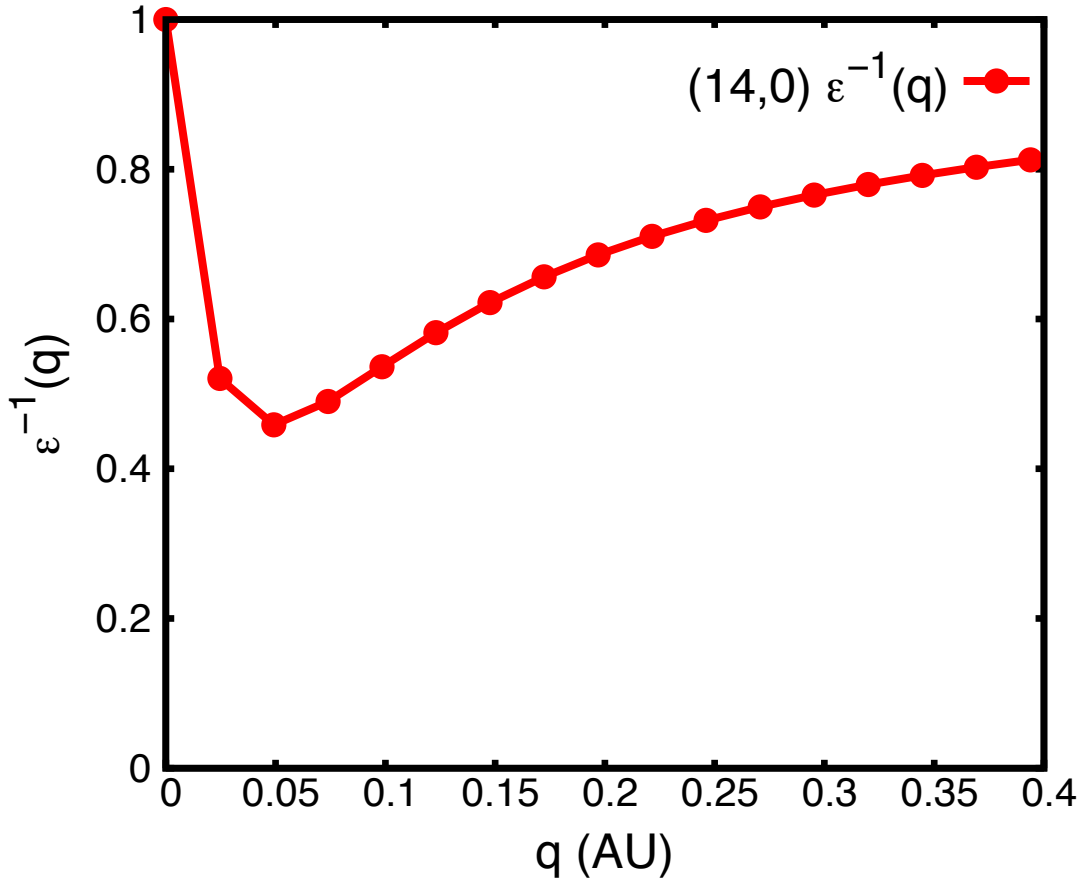
Absorption interpolates kernel over **q** with $W(\mathbf{q}) = \varepsilon^{-1}(\mathbf{q})\, v(\mathbf{q})$

$$\langle vc\mathbf{k}|K^{\mathrm{d}}|v'c'\mathbf{k}'\rangle = \sum_{\mathbf{GG'}} M^*_{c'c}(\mathbf{k},\mathbf{q},\mathbf{G})W_{\mathbf{GG'}}(\mathbf{q};0)M_{v'v}(\mathbf{k},\mathbf{q},\mathbf{G'})$$

Problem 1: Non-smooth behavior

(14, 0) carbon nanotube wire truncation

General for truncation: see BN tutorial



Problem 2: Divergent behavior

DOS inter/intra-band transitions gap

$$\chi_{\mathbf{GG'}}(\mathbf{q};0) = \sum_{n}^{\text{occ}} \sum_{n'}^{\text{emp}} \sum_{\mathbf{k}} M^{*}_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}) M_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G'}) \frac{1}{E_{n\mathbf{k}+\mathbf{q}} - E_{n'\mathbf{k}}}.$$

Head: **G** = 0, **G'** = 0
Wing: **G** = 0, **G'** ≠ 0
Wing': **G** ≠ 0, **G'** = 0
Body: **G** ≠ 0, **G'** ≠ 0

Cannot calculate at **q** = 0!

q^2/q^2 diverges

$\epsilon^{-1}_{\mathbf{GG'}}$	head	wing	wing'	body
Semiconductor	const	$\mathbf{q}$	$\mathbf{q}/q^2$	const
Metal	q^2	q^2	const	const

$W_{\mathbf{GG'}}$	head	wing	wing'	body
Semiconductor	$1/q^2$	$\mathbf{q}/q^2$	$\mathbf{q}/q^2$	const
Metal	const	const	const	const

q^2/q^2

Solution: Screening models

Calculate at $\mathbf{q_0} \approx 0.001$ in periodic direction
use to parametrize screening model

Sigma: Integrate over region around $\mathbf{q} = 0$

Kernel:
Interpolate
in parts

head wing, wing' body

$$\langle vc\mathbf{k}\,|K|\,v'c'\mathbf{k}'\rangle = \frac{a_{vc\mathbf{k}v'c'\mathbf{k}'}}{A(\mathbf{q})} + \frac{b_{vc\mathbf{k}v'c'\mathbf{k}'}}{B(\mathbf{q})} + \frac{c_{vc\mathbf{k}v'c'\mathbf{k}'}}{C(\mathbf{q})}$$

$\epsilon^{-1}_{\mathbf{GG'}}$	head	wing	wing'	body
Semiconductor	const	$\mathbf{q}$	$\mathbf{q}/q^2$	const
Metal	q^2	q^2	const	const

$W_{\mathbf{GG'}}$	head	wing	wing'	body
Semiconductor	$1/q^2$	$\mathbf{q}/q^2$	$\mathbf{q}/q^2$	const
Metal	const	const	const	const

Truncation of Coulomb potential

- GW and BSE utilize the Coulomb and screened Coulomb interaction

$$W = \varepsilon^{-1} V_c$$

- Long-range interactions make it computationally infeasible to increase lattice vectors until periodic images do not interact

Truncation Schemes within BerkeleyGW

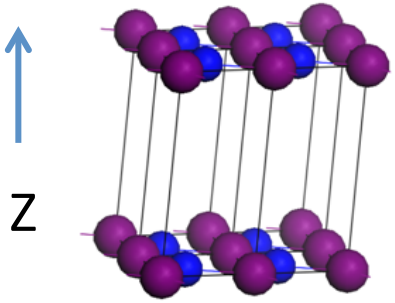
- Cell box: 0D
- Cell wire: 1D
- Cell slab: 2D
- Spherical: Define radius of truncation

$$v_t(\mathbf{r}) = \frac{\Theta(f(\mathbf{r}))}{r}$$

- **Cell truncation**: at half lattice vector length
  - Analytical form for Coulomb potential in k-space
- **Spherical truncation**: convenient, available in many packages

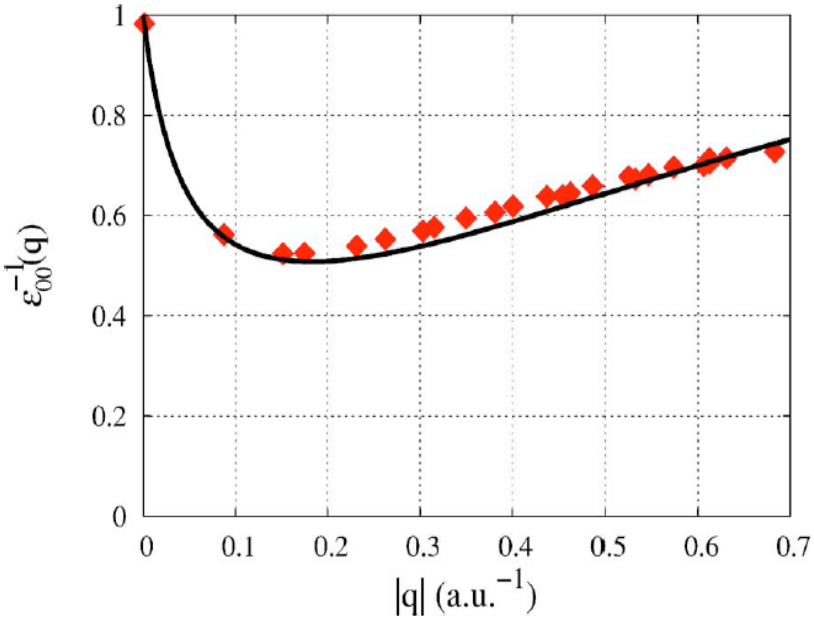
Example: BN sheets

$$V_c(\mathbf{r}) = \frac{\theta(z - L/2)}{|\mathbf{r}|} \longrightarrow V_c(\mathbf{k}) = \frac{4\pi}{|\mathbf{k}|^2}(1 - e^{-k_{xy}(L/2)}\cos(k_z(L/2))$$



Quasiparticle Correction	Separation length (a.u.)		
12x12x12 k-mesh	10	14	18
No Truncation	1.98	2.05	2.10
Truncation	**2.53**	**2.55**	**2.58**

- Convergence improved with truncation



Ismail-Beigi *PRB* **73** 233103 (2006)

Regular **k**-grids

Epsilon

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q};0) = \sum_{n}^{\text{occ}} \sum_{n'}^{\text{emp}} \sum_{\mathbf{k}} M^*_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}) M_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}') \frac{1}{E_{n\mathbf{k}+\mathbf{q}} - E_{n'\mathbf{k}}}.$$

where

$$M_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}) = \langle n\mathbf{k}+\mathbf{q}| \, e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \, |n'\mathbf{k}\rangle$$

Sigma

$$\langle n\mathbf{k}| \, \Sigma_{\text{SX}}(E) \, |n'\mathbf{k}\rangle = -\sum_{n''}^{\text{occ}} \sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} M^*_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G}) M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}')$$
$$\times \left[\epsilon_{\mathbf{G}\mathbf{G}'}\right]^{-1}(\mathbf{q}; E - E_{n''\mathbf{k}-\mathbf{q}}) v(\mathbf{q}+\mathbf{G}')$$

Kernel

$$\langle vc\mathbf{k}|K^{\text{d}}|v'c'\mathbf{k}'\rangle = \sum_{\mathbf{G}\mathbf{G}'} M^*_{c'c}(\mathbf{k},\mathbf{q},\mathbf{G}) W_{\mathbf{G}\mathbf{G}'}(\mathbf{q};0) M_{v'v}(\mathbf{k},\mathbf{q},\mathbf{G}')$$

$$\epsilon^{-1}(\mathbf{q}) \text{ for } \mathbf{q} = \mathbf{k} - \mathbf{k}'.$$

k-grids and bands

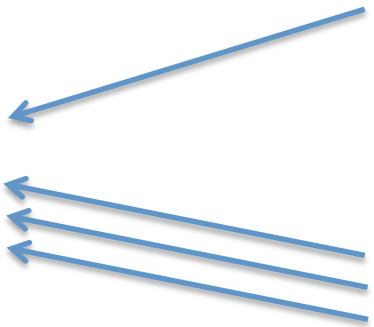
recommended approach

	k-grid	# bands	Comments
SCF	Uniform, 0.5 shift	occupied	as usual in DFT
WFN	Uniform, 0.5 shift	many	
WFNq	WFN + **q**-shift	occupied	
epsilon.inp **q**-points	WFN but no shift, $\mathbf{q}_0$	many	bands to sum over
WFN_inner	WFN but no shift	many	bands to sum over
sigma.inp **k**-points	subset of WFN_inner	few	can choose to calculate Sigma just for bands of interest
WFN_co	WFN_inner	few	
WFN_fi (absorption)	Uniform, random shift	few	
WFNq_fi	WFN_fi + **q**-shift	occupied	
WFN_fi (inteqp)	anything	few	whatever is of interest

epsilon.inp

Semiconductors

```
begin qpoints
   0.000000     0.000000     0.005000    1.0    1
   0.000000     0.000000     0.062500    1.0    0
   0.000000     0.000000     0.125000    1.0    0
   0.000000     0.000000     0.187500    1.0    0
 …
end
```



eps0mat:

$$\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}_0)$$

epsmat:

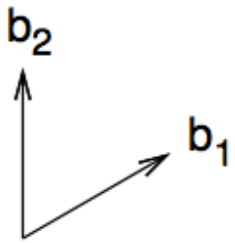
$$\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q} \neq \mathbf{q}_0)$$

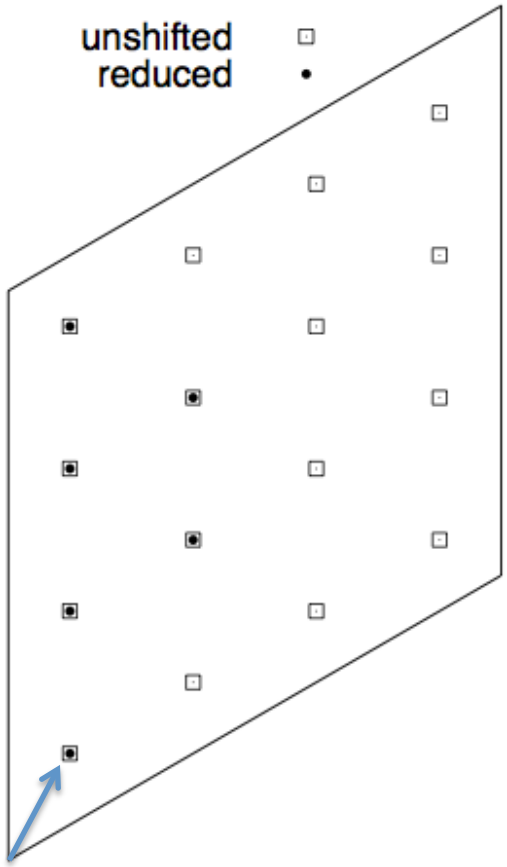
k-grid construction: 4×4 grid for graphene

(0.5, 0.5) Monkhorst-Pack shift

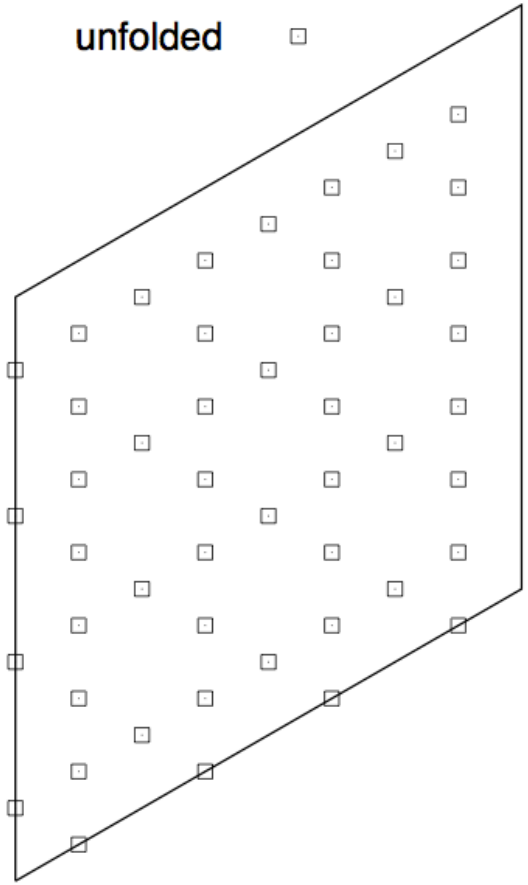
`kgrid.x`

Uniform -> unfold -> shift with **q** -> reduce





(0.5, 0.5)



Unfolding gives more points!

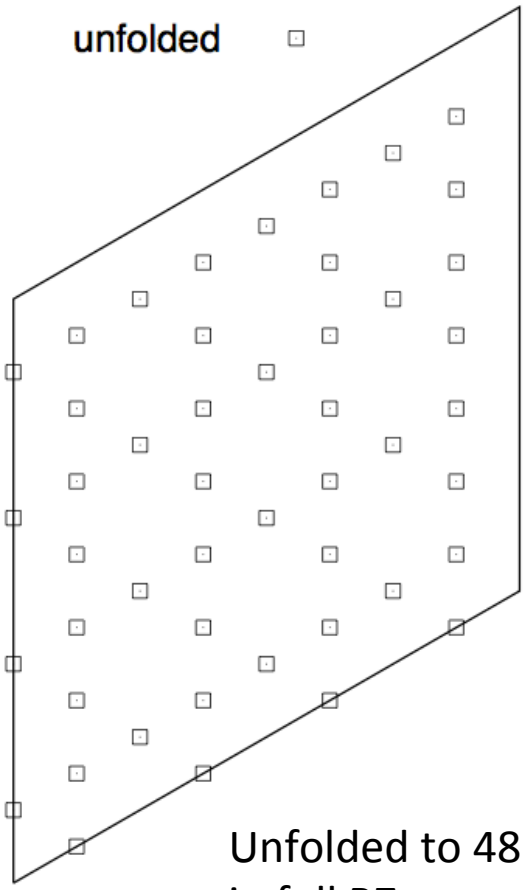
Main grid (WFN)
16 in full BZ
Reduced to 6

Unfolded to 48 in full BZ

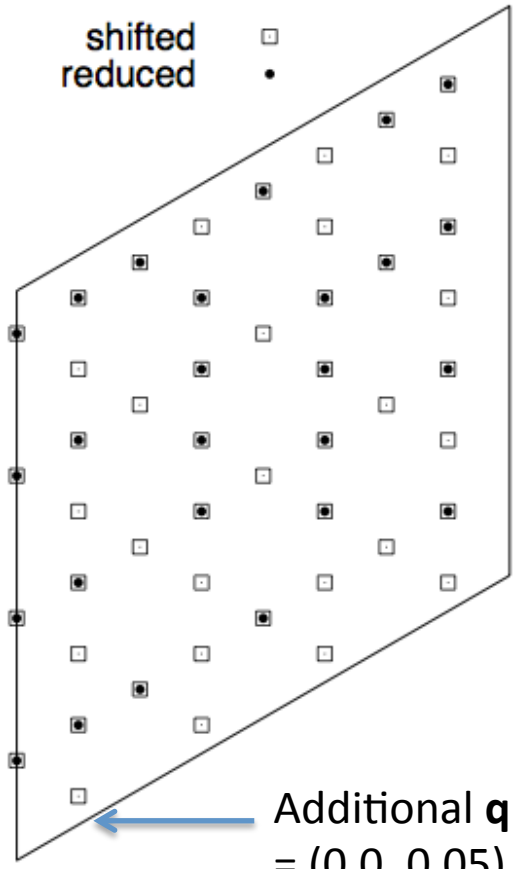
k-grid construction: 4×4 grid for graphene

`kgrid.x`

Uniform -> unfold ->
shift with **q** -> reduce



Unfolded to 48
in full BZ



Additional **q**
= (0.0, 0.05)

Shifted grid (WFNq)
48 in full BZ
Reduced to 26

Unfolding and breaking
symmetry gives more points!

Degeneracy

Epsilon, Sigma: symmetry of Hamiltonian

$$\langle n\mathbf{k}|\,\Sigma_{\mathrm{SX}}(E)\,|n'\mathbf{k}\rangle = -\sum_{n''}^{\mathrm{occ}}\sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} M^*_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G})M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}')$$
$$\times\left[\epsilon_{\mathbf{G}\mathbf{G}'}\right]^{-1}(\mathbf{q};E-E_{n''\mathbf{k}-\mathbf{q}})v(\mathbf{q}+\mathbf{G}')$$

Absorption: symmetry of e-h basis

$$\left(E^{\mathrm{QP}}_{c\mathbf{k}}-E^{\mathrm{QP}}_{v\mathbf{k}}\right)A^S_{vc\mathbf{k}}+\sum_{v'c'\mathbf{k}'}\left\langle vc\mathbf{k}|K^{\mathrm{eh}}|v'c'\mathbf{k}'\right\rangle=\Omega^S A^S_{vc\mathbf{k}}$$

Summing over only some of a degenerate space will break symmetry.
Degeneracy in mean-field => broken in *GW*!
Results depends on arbitrary linear combinations in mean-field. Not reproducible!
Incorrect oscillator strengths in absorption!

Degeneracy check utility

```
$ degeneracy_check.x WFN

Reading eigenvalues from file WFN
Number of spins:                 1
Number of bands:                35
Number of k-points:              8

== Degeneracy-allowed numbers of bands (for epsilon and sigma) ==
             4
             8
            14
            18
            20
            32
Note: cannot assess whether or not highest band     35 is degenerate.
```

So, use `number_bands 32` in Epsilon.

Real or complex flavor?

e.g. bin/epsilon.real.x, bin/epsilon.cplx.x

Complex is general, but real is faster, uses less memory and disk space

Real: only with inversion symmetry about the origin $u(-\mathbf{r}) = au(\mathbf{r})$

and time-reversal symmetry $u^*(\mathbf{r}) = bu(\mathbf{r})$

a, b each equal to ± 1

What breaks time-reversal? Magnetic fields, spin-polarization, spinors
Plane-wave codes generally just use complex wavefunctions.
Conditions for reality depends on the basis! Real-space: *k* = 0, time-reversal.

Real output not implemented in Octopus yet.

There are many convergence parameters in a GW calculations : convergence with each must be checked

Screened cutoff

Empty bands (dielectric matrix)

$$\chi_{\mathbf{GG'}}(\mathbf{q},0) = \sum_{n}^{\text{occ}} \sum_{n'}^{\text{emp}} \sum_{\mathbf{k}} M^*_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}) M_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}') \frac{1}{E_{n\mathbf{k}+\mathbf{q}} - E_{n'\mathbf{k}}}$$

q-grid

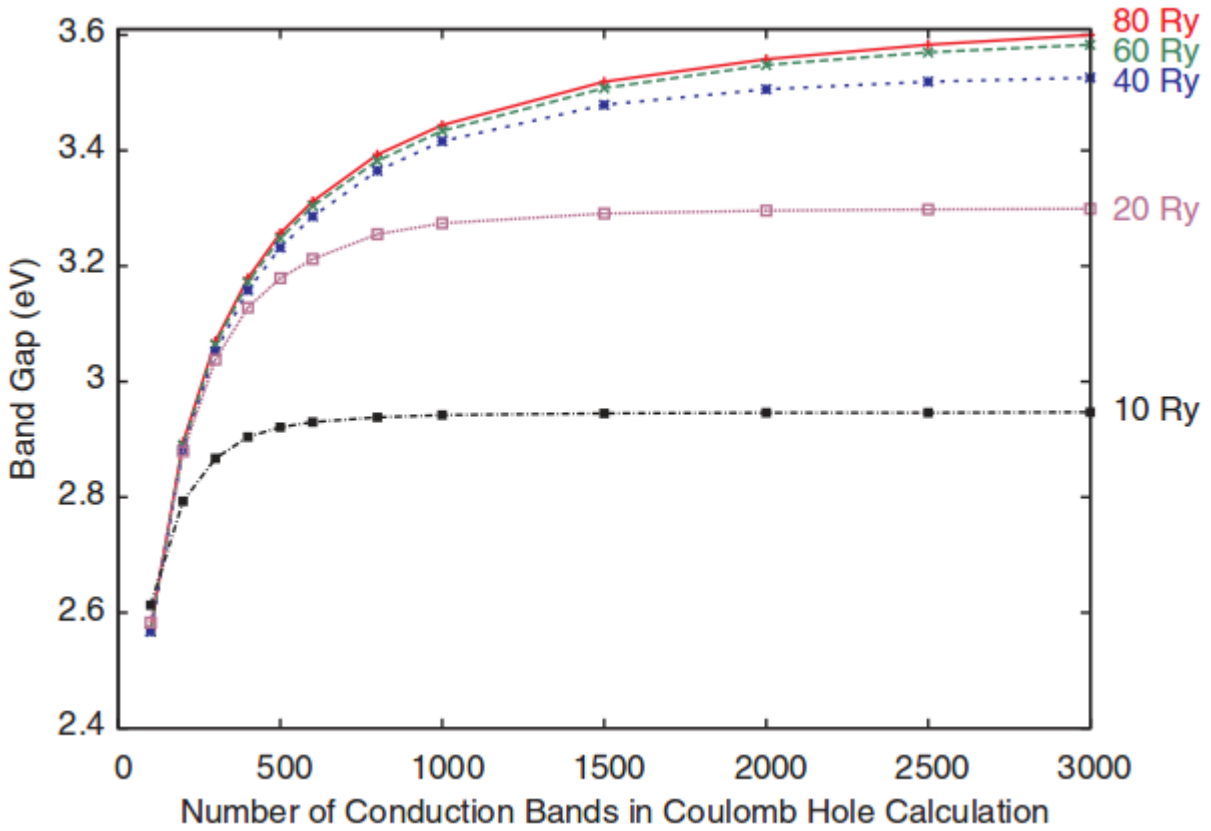
Bands in CH summation (sigma)

$$\langle n\mathbf{k}| \Sigma_{\text{CH}}(E) |n'\mathbf{k}\rangle = \frac{1}{2} \sum_{n''} \sum_{\mathbf{qGG'}} M^*_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G}) M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}') \times \frac{\Omega^2_{\mathbf{GG'}}(\mathbf{q})\,(1 - i\tan\phi_{\mathbf{GG'}}(\mathbf{q}))}{\tilde{\omega}_{\mathbf{GG'}}(\mathbf{q})\,(E - E_{n''\mathbf{k}-\mathbf{q}} - \tilde{\omega}_{\mathbf{GG'}}(\mathbf{q}))}\, v(\mathbf{q}+\mathbf{G}')$$

$$M_{nn'}(\mathbf{k},\mathbf{q},\mathbf{G}) = \langle n\mathbf{k}+\mathbf{q}|\, e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\, |n'\mathbf{k}\rangle$$

Wavefunction cutoff (matrix elements)

Coupled convergence parameters



B. Shih et al., ZnO

Octopus interface to BerkeleyGW

Real space transformed to plane-waves for GW.

Can only produce complex wavefunctions currently.

Periodic systems must use orthogonal unit cells (*i.e.* not hcp, fcc, …)
so build a supercell to match this condition.

Can treat rigorously finite systems, unlike plane-wave codes.

Domain parallelization for real-space scales better than plane waves.

Not yet in released version of Octopus!
Hence, warnings about experimental features.

The tutorial

Two examples:
(1) hexagonal boron nitride sheet
(2) benzene molecule

Today: GW
Tomorrow: Bethe-Salpeter equation

Instructions at
http://www.tddft.org/programs/octopus/wiki/index.php/Tutorial:BerkeleyGW

Get your Hopper account if you didn't yet!