Practical calculations of semiconductors and metals

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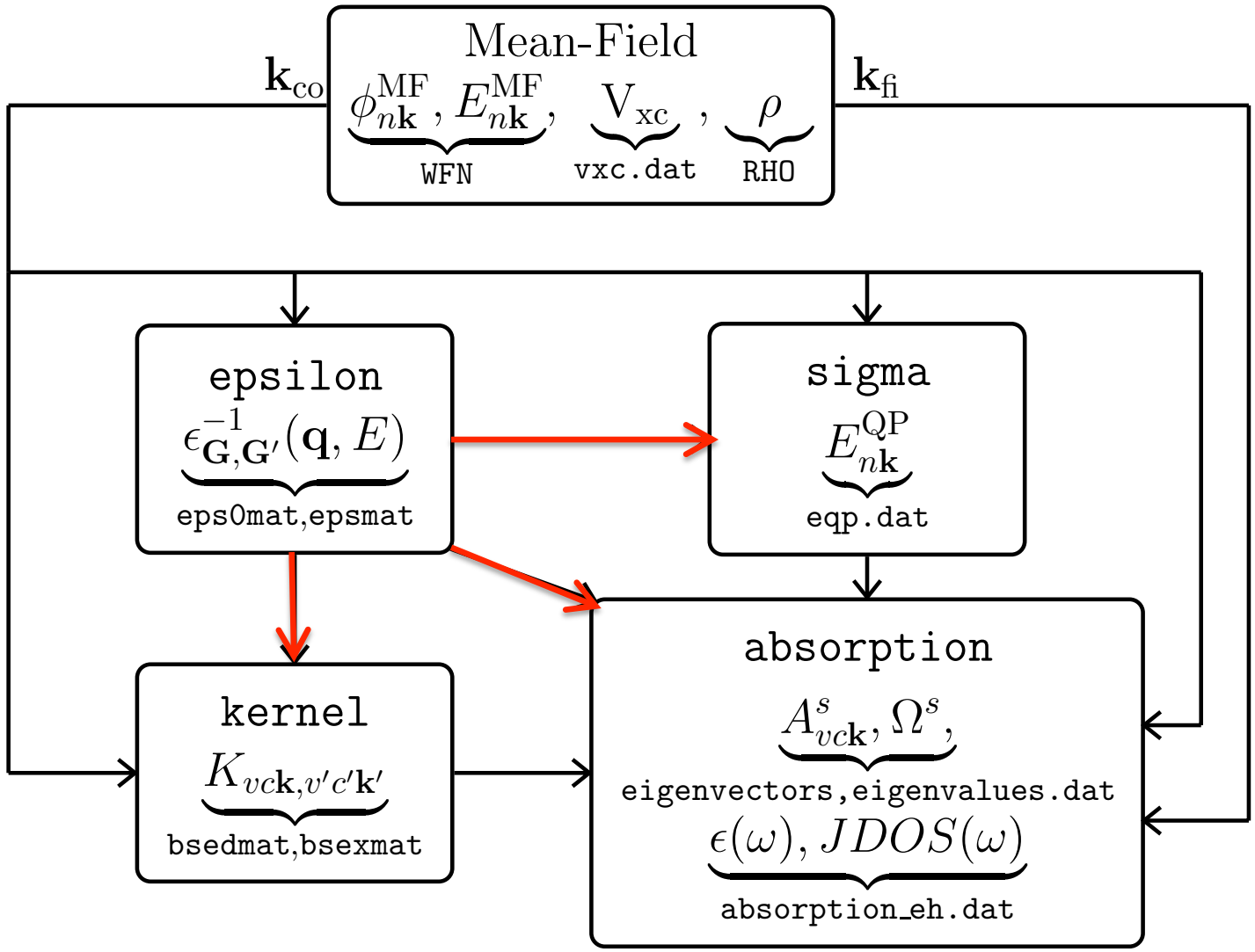
Outline

1. Screening models for Epsilon
2. Construction of **k**-grids
3. Special treatment for metals in Epsilon
4. Symmetry and degeneracy
5. Linearizing the Dyson equation
6. Real and complex version

Screening models: How do we use ε?



Screening models: How do we use ε?

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

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

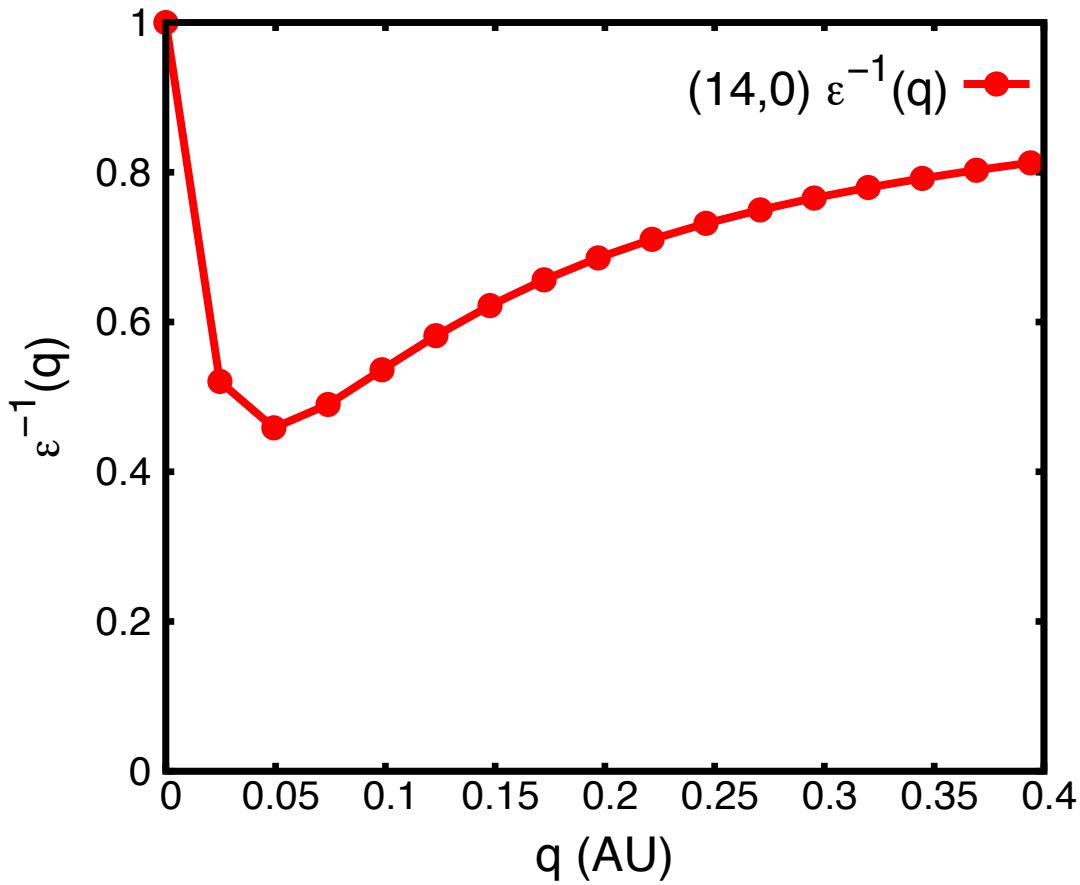
Absorption interpolates kernel over **q** with W(**q**) = $\varepsilon^{-1}(\mathbf{q})$ v(**q**)

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

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 $\mathbf{q_0} \approx 0.001$; use to parametrize screening model (*note: anisotropic materials need multiple directions*)

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

Kernel: Interpolate in parts

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

$\epsilon^{-1}_{\mathbf{GG}'}$	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: different screening models

$$v_t(\mathbf{r}) = \frac{\Theta(f(\mathbf{r}))}{r}$$ wire, slab, cell

$\mathbf{q_0} \approx 0$ should be in periodic direction, or actually 0 for molecule

$\epsilon^{-1}_{\mathbf{GG'}}$	head	wing	wing′	body
Semiconductor	1	$\mathbf{q}\epsilon^{-1}_{0,0}(\mathbf{q})$	$\mathbf{q}\epsilon^{-1}_{0,0}(\mathbf{q})\,v(\mathbf{q})$	const
Metal	$1/v(\mathbf{q})$	$1/v(\mathbf{q})$	const	const

$W_{\mathbf{GG'}}$	head	wing	wing′	body
Semiconductor	$\epsilon^{-1}_{0,0}(\mathbf{q})\,v(\mathbf{q})$	$\mathbf{q}\epsilon^{-1}_{0,0}(\mathbf{q})\,v(\mathbf{q})$	$\mathbf{q}\epsilon^{-1}_{0,0}(\mathbf{q})\,v(\mathbf{q})$	const
Metal	const	const	const	const

Regular **k**-grids

Epsilon

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

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

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

Kernel

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

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

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

Special treatment for metals

Coefficients depend critically on sampling DOS at Fermi surface for intraband transitions.

$\epsilon^{-1}_{\mathbf{GG}'}$	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

Two separate runs of Epsilon

eps0mat: $\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q}_0)$

WFN = WFNq
only a small number of bands for intra-band transitions around Fermi surface
very fine: grid spacing is $\mathbf{q}_0$ *e.g.* grid = 32 × 32 × 32 unshifted, $\mathbf{q}_0$ = (0, 0, 1/32)

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

WFN = WFNq. unshifted, many bands, ordinary fineness. *e.g.* grid = 12 × 12 × 12.

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:

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

Metals

```
begin qpoints
  0.000000000  0.000000000  0.031250000 1.0 2
end
```

eps0mat:

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

```
begin qpoints
  0.000000000  0.000000000  0.083333333 1.0 0
  0.000000000  0.000000000  0.166666667 1.0 0
  0.000000000  0.000000000  0.250000000 1.0 0
…
end
```

epsmat:

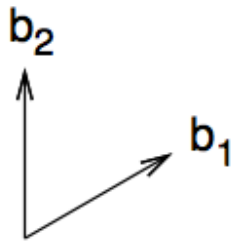
$$\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q} \neq \mathbf{q}_0)$$

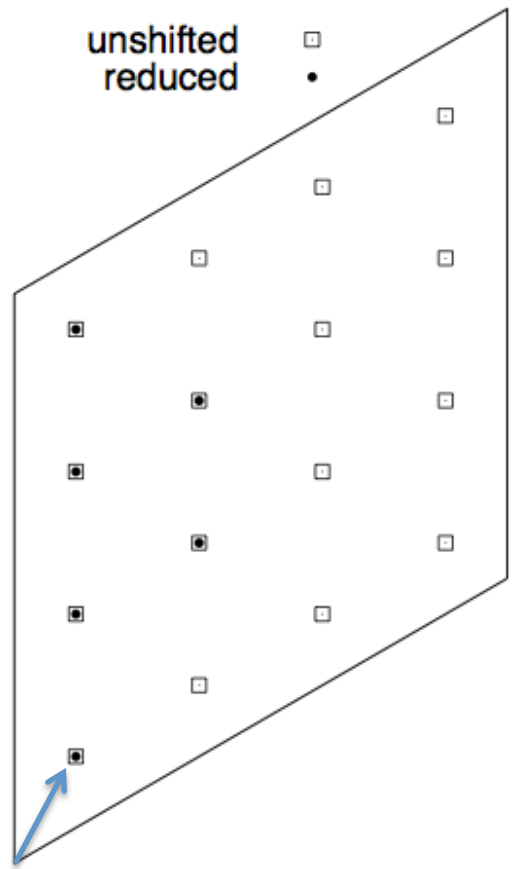
k-grid construction: 4×4 grid for graphene

(0.5, 0.5) Monkhorst-Pack shift

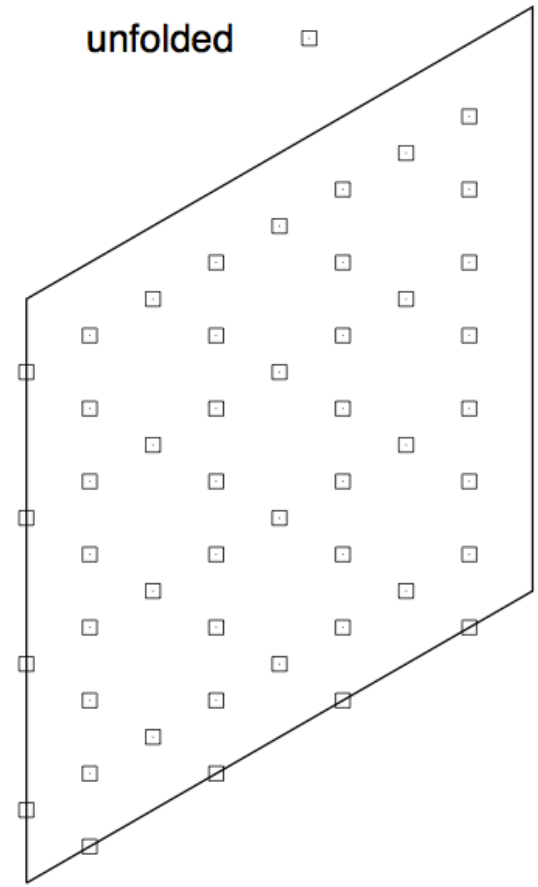
`kgrid.x`

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





(0.5, 0.5)



Unfolding gives more points!

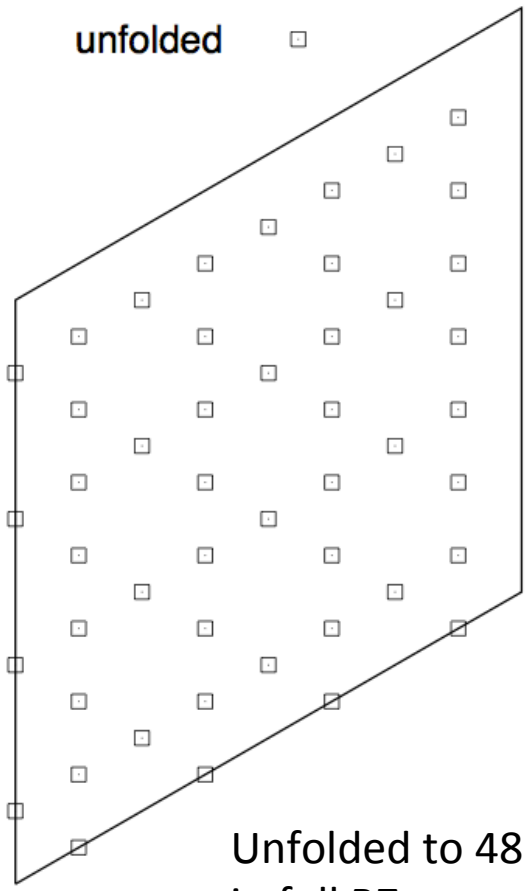
Main grid (WFN)
16 in full BZ
Reduced to 6

Unfolded to 48 in full BZ

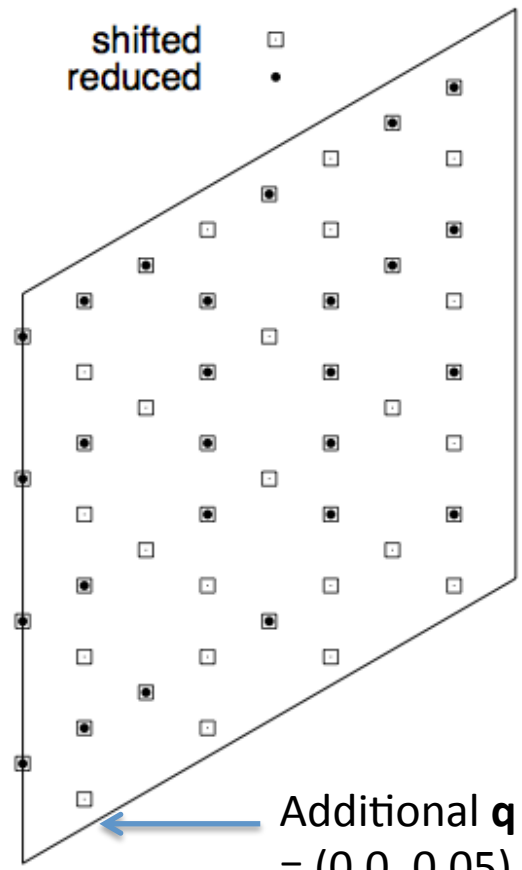
k-grid construction: 4×4 grid for graphene

`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 in DFT/GW/BSE

Degeneracy is from symmetry.

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic	
A_1	1	1	1	1	1		$x^2+y^2+z^2$	
A_2	1	1	1	-1	-1			
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$	doubly degenerate space
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)		triply degenerate space
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)	triply degenerate space

Degeneracy

Epsilon, Sigma: symmetry of Hamiltonian

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

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.

Solving Dyson's equation

$$E_{n\mathbf{k}}^{\mathrm{QP}} = E_{n\mathbf{k}}^{\mathrm{MF}} + \langle \psi_{n\mathbf{k}} | \Sigma(E_{n\mathbf{k}}^{\mathrm{QP}}) - \Sigma^{\mathrm{MF}} | \psi_{n\mathbf{k}} \rangle$$

How can we solve when we don't know E^{QP} yet?

(1) eqp0: evaluate at E^{MF}.

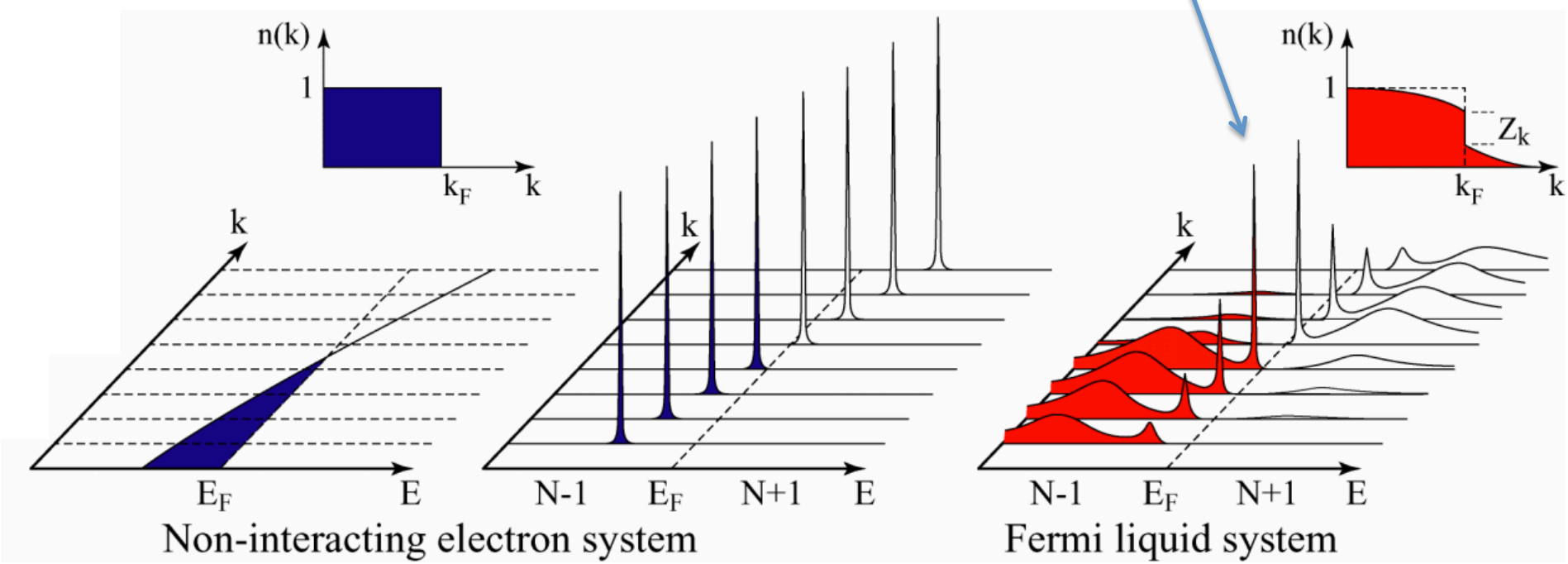
(2) eqp1: solve linearized approximation (Newton's Method)

$$E_{n\mathbf{k}}^{\mathrm{QP}} = E_{n\mathbf{k}}^{0} + \frac{d\Sigma/dE}{1 - d\Sigma/dE}(E_{n\mathbf{k}}^{0} - E_{n\mathbf{k}}^{\mathrm{MF}})$$

Quasiparticle renormalization factor *Z*

$$E_{n\mathbf{k}}^{\mathrm{QP}} = E_{n\mathbf{k}}^{0} + \frac{d\Sigma/dE}{1 - d\Sigma/dE}(E_{n\mathbf{k}}^{0} - E_{n\mathbf{k}}^{\mathrm{MF}}) \qquad Z = \frac{1}{1 - d\Sigma/dE}$$

Between 0 and 1
Weight in QP peak



A. Damascelli, Z. Hussain, Z.-X Shen, Rev. Mod. Phys. **75**, 473 (2003)

Real or complex flavor?

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

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

Plane-wave expansion:

$$u(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \longrightarrow u_{\mathbf{G}} = c u_{\mathbf{G}}^*$$

Choose c = 1 for real
(or c = -1 for imaginary)

Same for density and Vxc, except no need for time-reversal. $\rho(\mathbf{r}) = \rho^*(\mathbf{r})$.

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.