Practical calculations with the GW approximation and Bethe-Salpeter equation in BerkeleyGW

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BerkeleyGW

octopus

NERSC

Benasque, Spain
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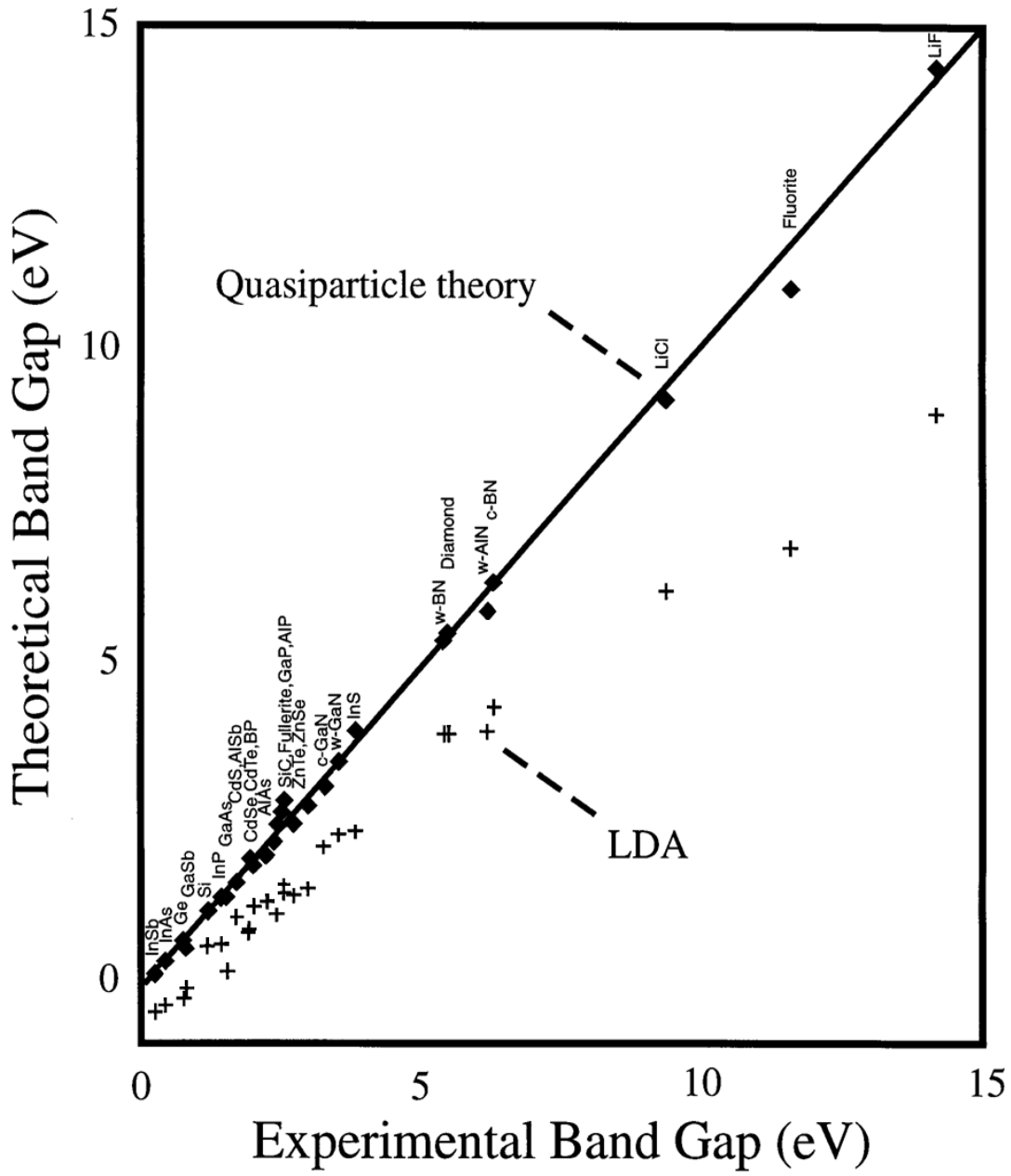
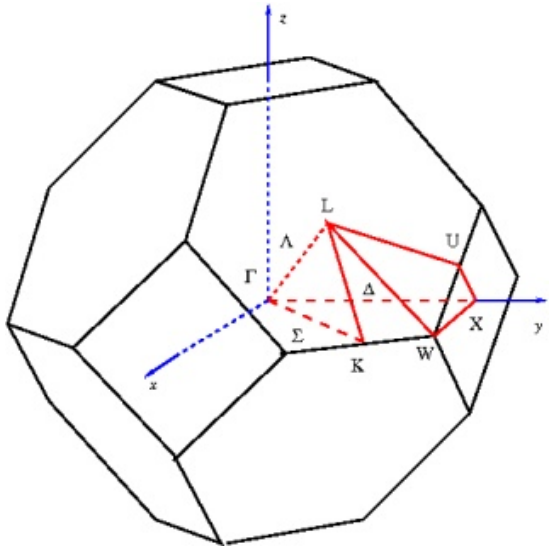
Band gaps: DFT-LDA and GW

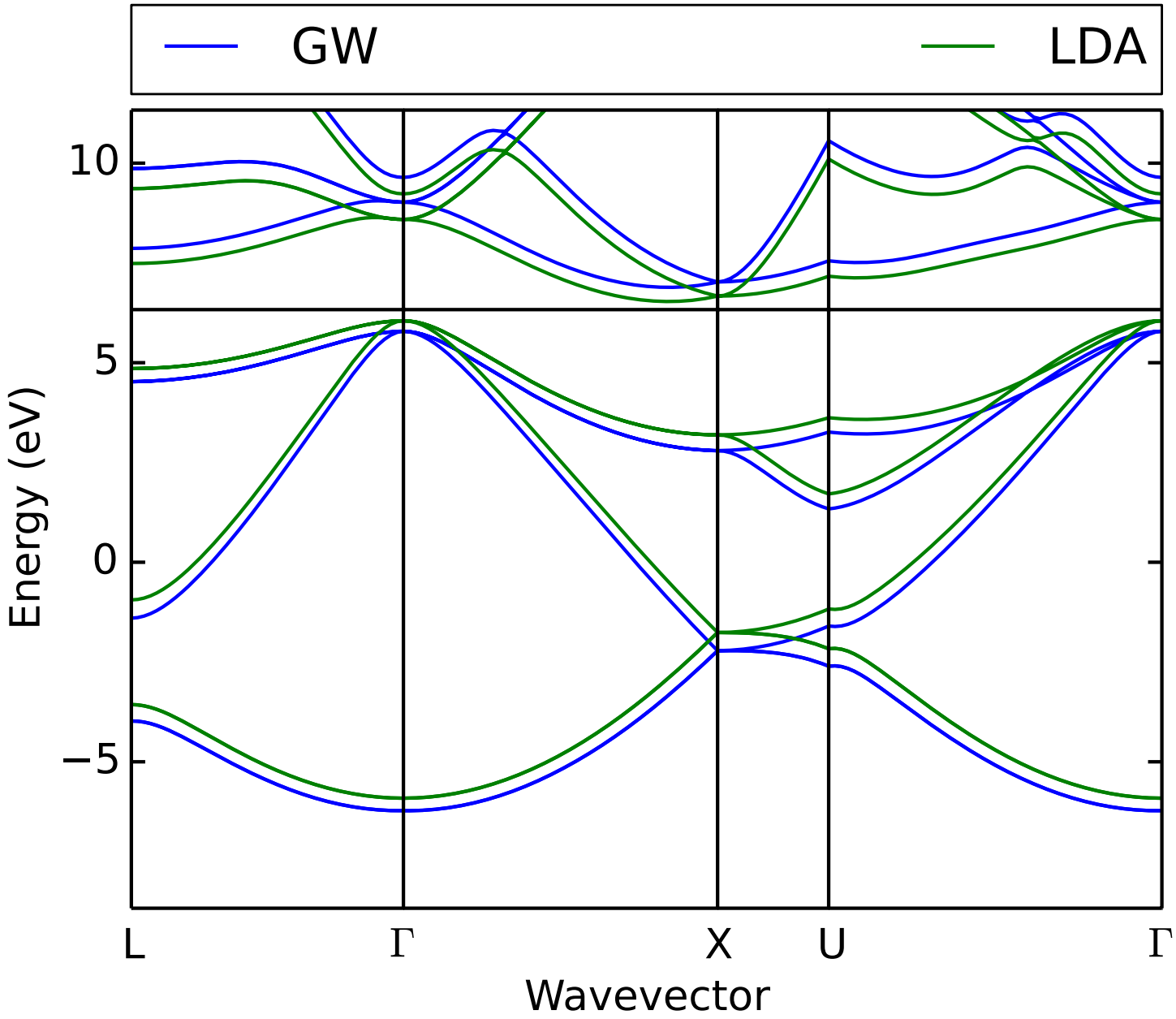
Materials:

InSb, InAs
Ge
GaSb
Si
InP
GaAs
CdS
AlSb, AlAs
CdSe, CdTe
BP
SiC
C_{60}
GaP
AlP
ZnTe, ZnSe
c-GaN, w-GaN
InS
w-BN, c-BN
diamond
w-AlN
LiCl
Fluorite
LiF



Silicon interpolated bandstructure

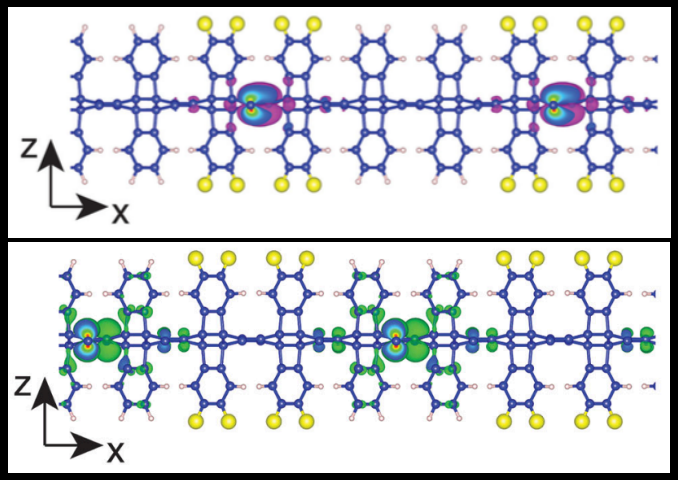


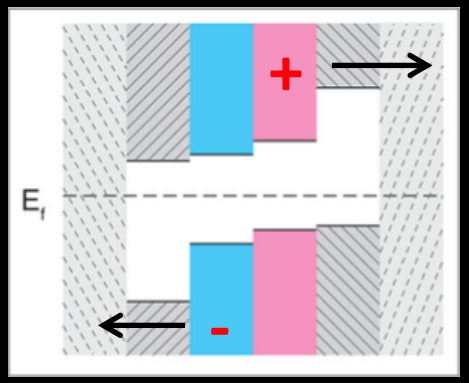


GW/Bethe-Salpeter for graphene-based PV

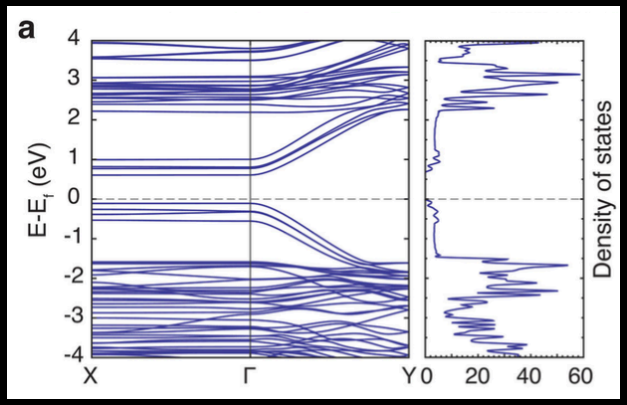
valence

conduction

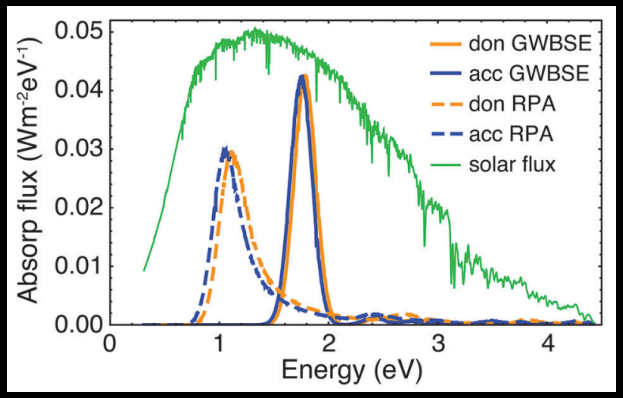


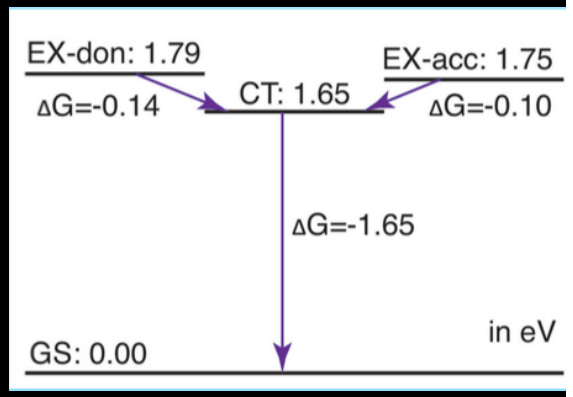


Band structure and density of states

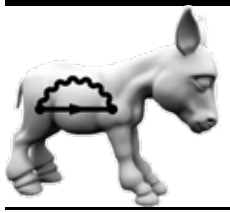


Excitons (electron-hole pairs) from Bethe-Salpeter equation





H. Li, D. A. Strubbe, and Jeffrey C. Grossman, *Adv. Funct. Mater.* **25**, 5199 (2015)



BerkeleyGW

Preview: GW approximation/Bethe-Salpeter eqn

Start with wavefunctions and energies from DFT as mean field

Add perturbation: difference between Vxc and true exchange-correlation

GW self-energy: single-electron energy levels (band structure)

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ion}} + V_{\text{H}} + \Sigma(E^{\text{QP}}_{n\mathbf{k}})\right]\psi^{\text{QP}}_{n\mathbf{k}} = E^{\text{QP}}_{n\mathbf{k}}\psi^{\text{QP}}_{n\mathbf{k}}$$

Bethe-Salpeter equation: electron-hole interaction for optical properties

$$\left(E^{\text{QP}}_{c\mathbf{k}} - E^{\text{QP}}_{v\mathbf{k}}\right)A^S_{vc\mathbf{k}} + \sum_{v'c'\mathbf{k}'}\left\langle vc\mathbf{k}\middle|K^{\text{eh}}\middle|v'c'\mathbf{k}'\right\rangle = \Omega^S A^S_{vc\mathbf{k}} \qquad \Psi(\mathbf{r}_e,\mathbf{r}_h) = \sum_{\mathbf{k},c,v} A^S_{vc\mathbf{k}}\psi_{\mathbf{k},c}(\mathbf{r}_e)\psi^*_{\mathbf{k},v}(\mathbf{r}_h)$$

BerkeleyGW

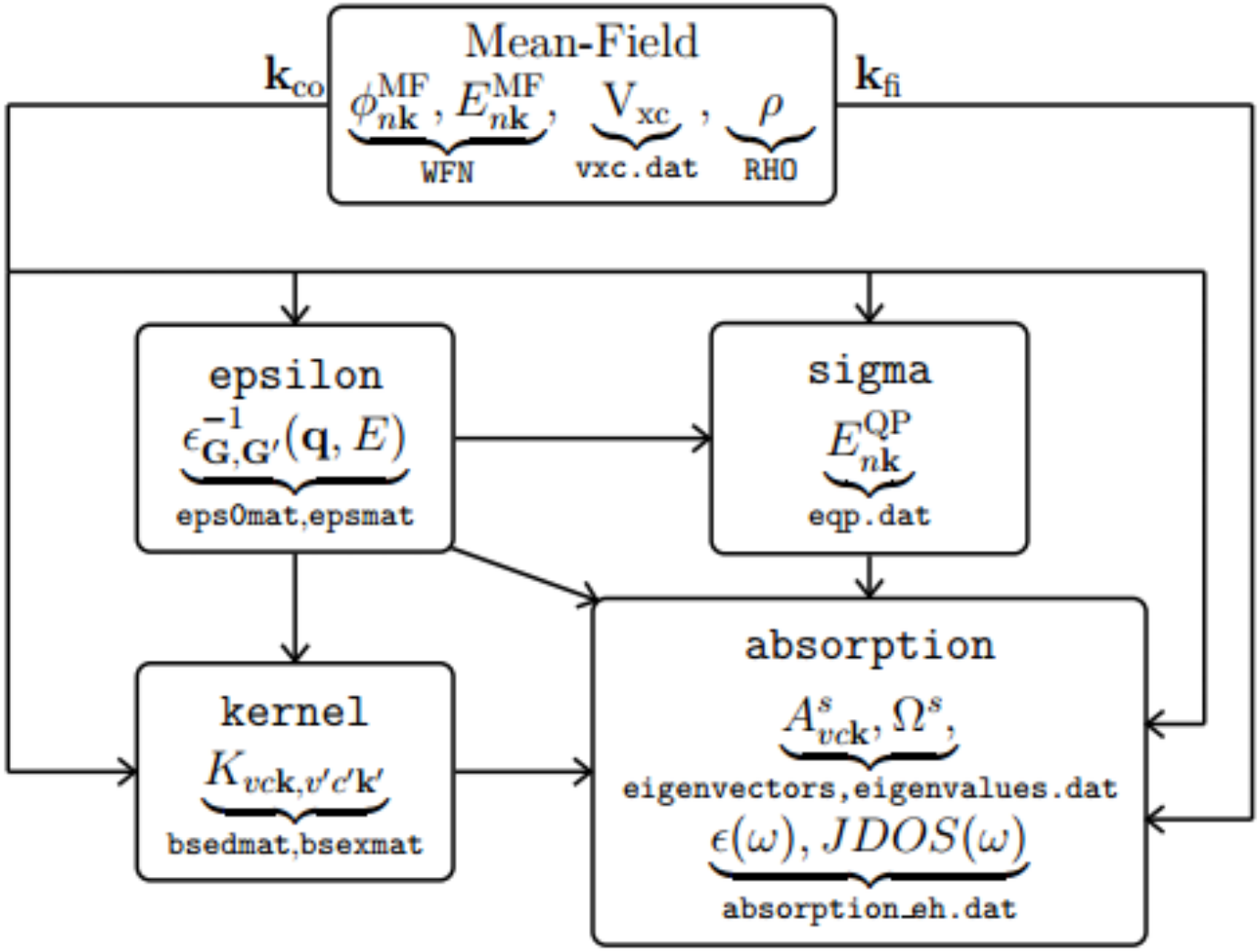
widely used massively parallel code
(~1000s of atoms)
www.berkeleygw.org

J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, *Comput. Phys. Comm.* **183**, 1269 (2012)

Why Use BerkeleyGW

- Supports a large set of Mean-Field codes: PARATEC, Quantum ESPRESSO, ABINIT, 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, FFTW3, LAPACK, SCALAPACK, OpenMP, HDF5)
- 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

Full-Frequency vs. Plasmon Pole calculations

$$\langle n\mathbf{k}|\,\Sigma_{\mathrm{CH}}(E)\,|n'\mathbf{k}\rangle = \frac{i}{2\pi}\sum_{n''}\sum_{\mathbf{q}\mathbf{G}\mathbf{G}'} M^{*}_{n''n}(\mathbf{k},-\mathbf{q},-\mathbf{G})M_{n''n'}(\mathbf{k},-\mathbf{q},-\mathbf{G}') \quad (20)$$

$$\times \int_0^\infty dE' \, \frac{\left[\epsilon^{\mathrm{r}}_{\mathbf{G}\mathbf{G}'}\right]^{-1}(\mathbf{q};E') - \left[\epsilon^{\mathrm{a}}_{\mathbf{G}\mathbf{G}'}\right]^{-1}(\mathbf{q};E')}{E - E_{n''\mathbf{k}-\mathbf{q}} - E' + i\delta} \, v(\mathbf{q}+\mathbf{G}')$$

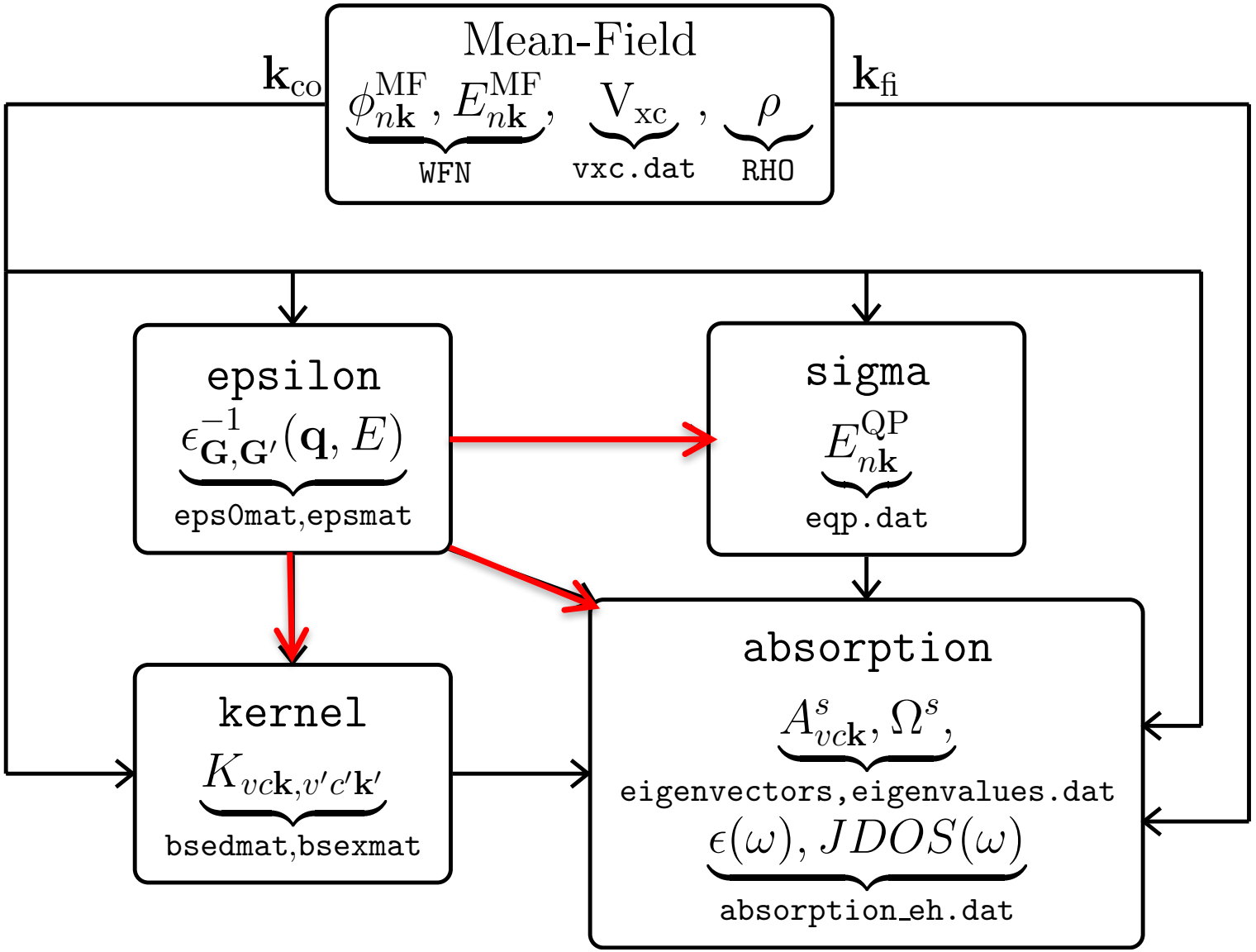
Plasmon pole is significantly faster. The integral over frequencies can be performed analytically if assume the dielectric response is dominated by a single plasmon pole.

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

Practical issues for *GW*

1. Screening models for Epsilon
2. Construction of **k**-grids
3. Symmetry and degeneracy
4. Real and complex version
5. Solving Dyson's equation
6. Convergence

Screening models: How do we use ε?



Screening models: How do we use ε?

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

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

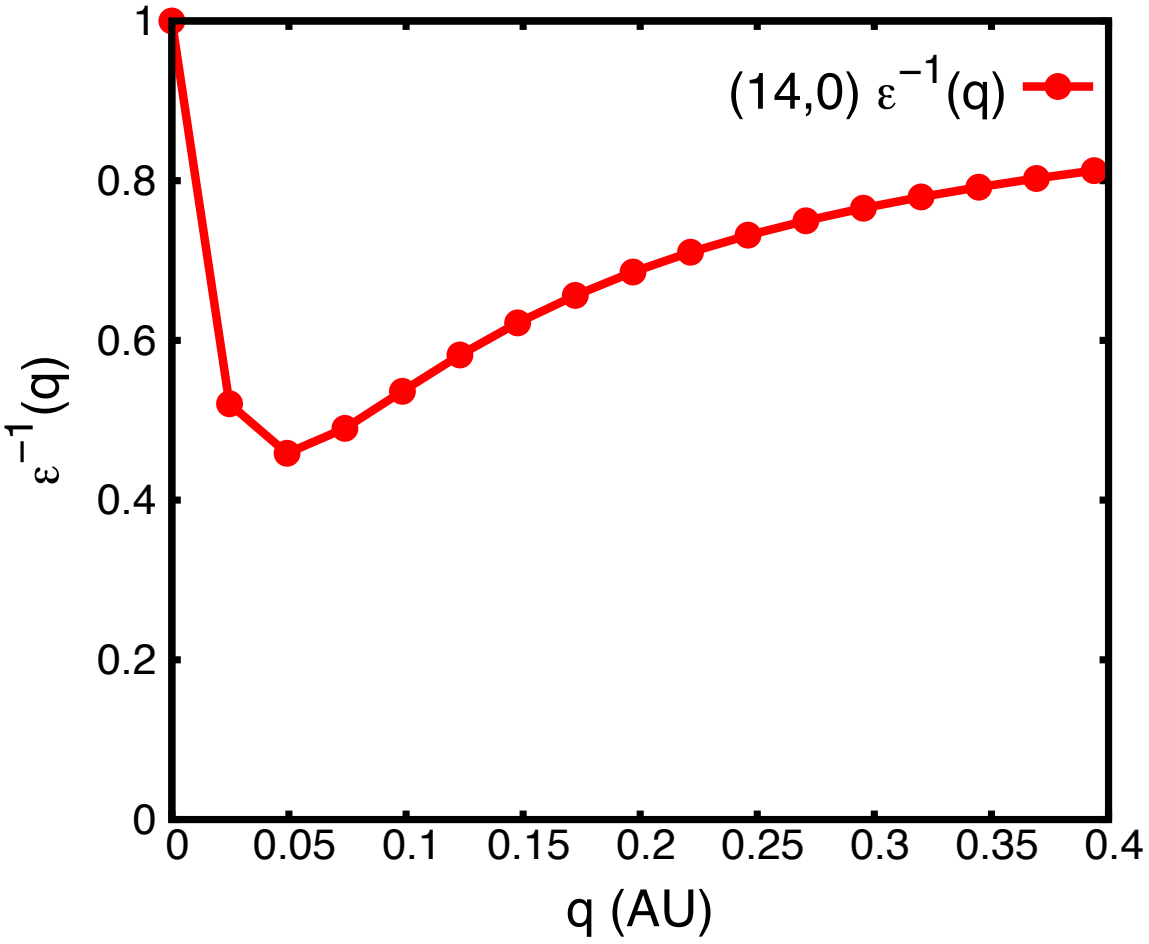
Absorption interpolates kernel over **q** with $W(\mathbf{q}) = \varepsilon^{-1}(\mathbf{q})\, v(\mathbf{q})$

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

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

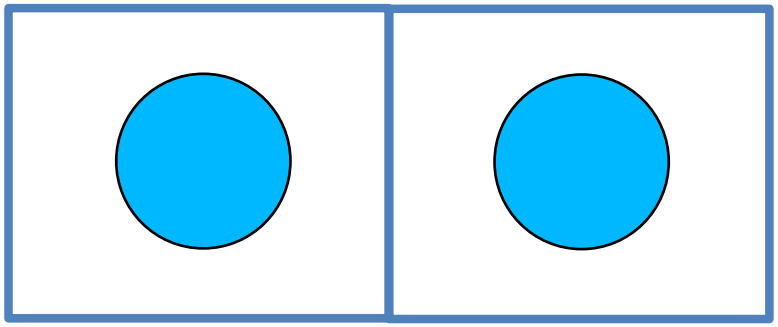
$$\langle vc\mathbf{k}|K|v'c'\mathbf{k}'\rangle = \frac{a_{vc\mathbf{k}v'c'\mathbf{k}'}}{A(\mathbf{q})} + \frac{b_{vc\mathbf{k}v'c'\mathbf{k}'}}{B(\mathbf{q})} + \frac{c_{vc\mathbf{k}v'c'\mathbf{k}'}}{C(\mathbf{q})}$$

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

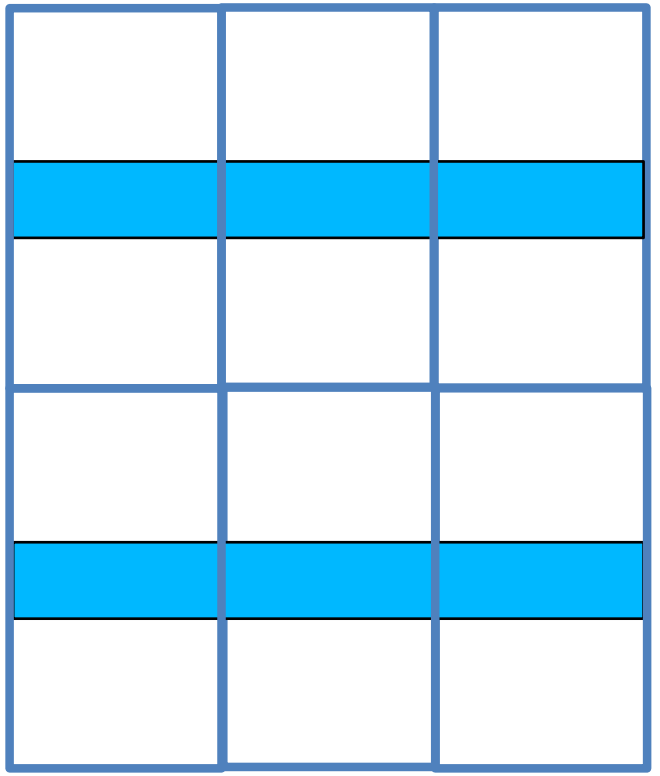
Truncation for non- or partially periodic systems

Periodicity in 0, 1, 2, or 3 dimensions. Eliminate spurious image interactions.



Cell (for molecule)

Wire (for nanotube or nanowire)



Slab (for graphene or surface)

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.
- Rule of thumb: non-periodic direction should include 99% of density

Truncation Schemes within BerkeleyGW

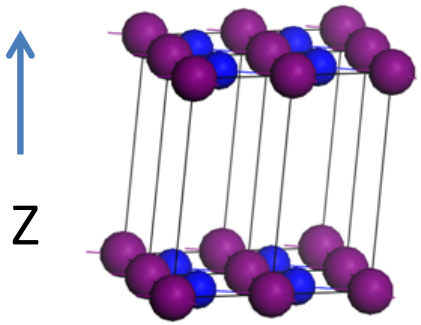
- Cell box: 0D
- Cell wire: 1D
- Cell slab: 2D
- Spherical: Define radius of truncation

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

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

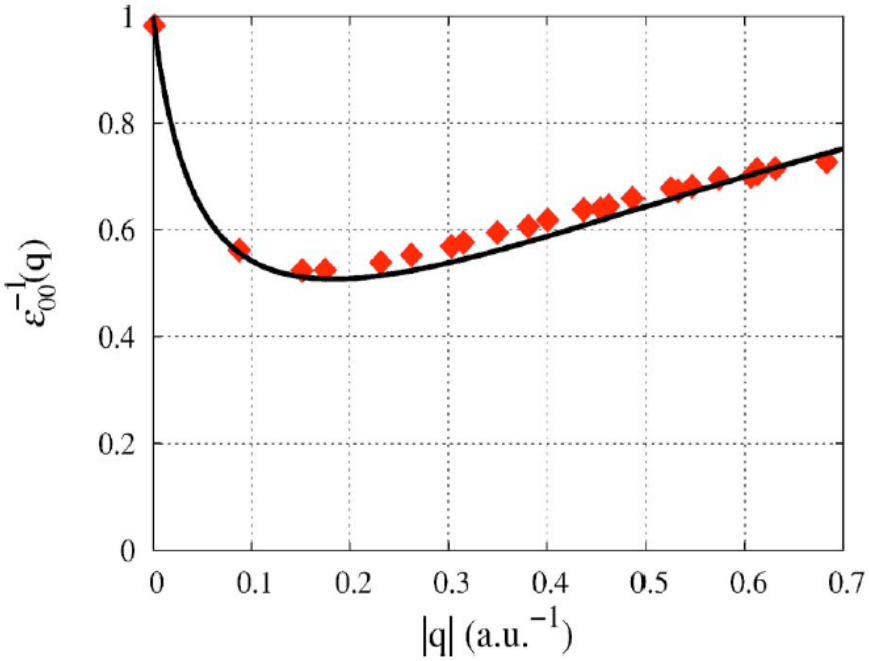
Example: BN sheets

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



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

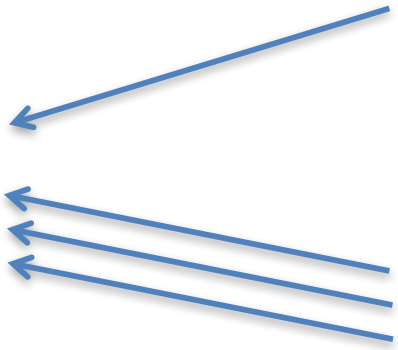
recommended approach

	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:

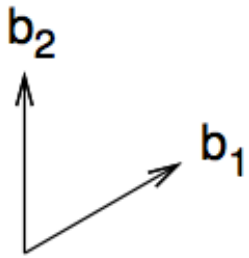
$$\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q} \neq \mathbf{q}_0)$$

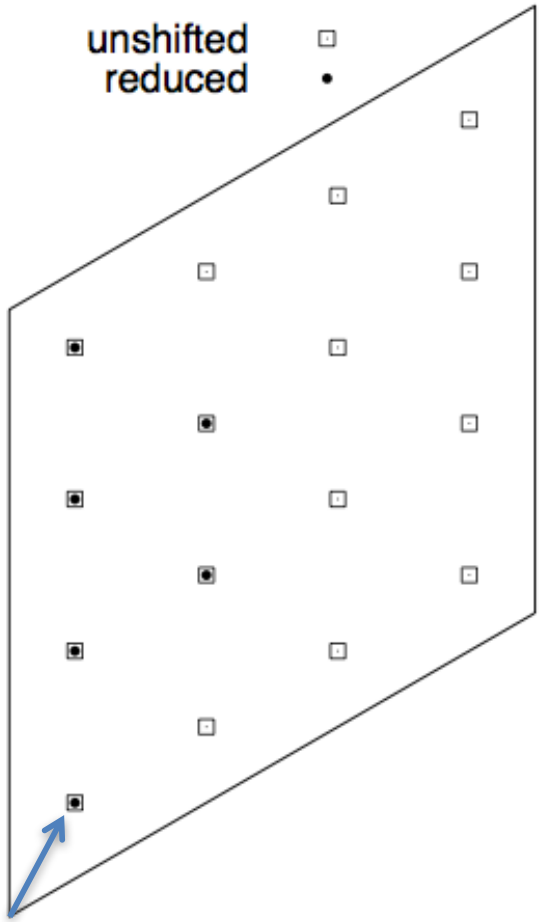
k-grid construction: 4×4 grid for graphene

(0.5, 0.5) Monkhorst-Pack shift

`kgrid.x`

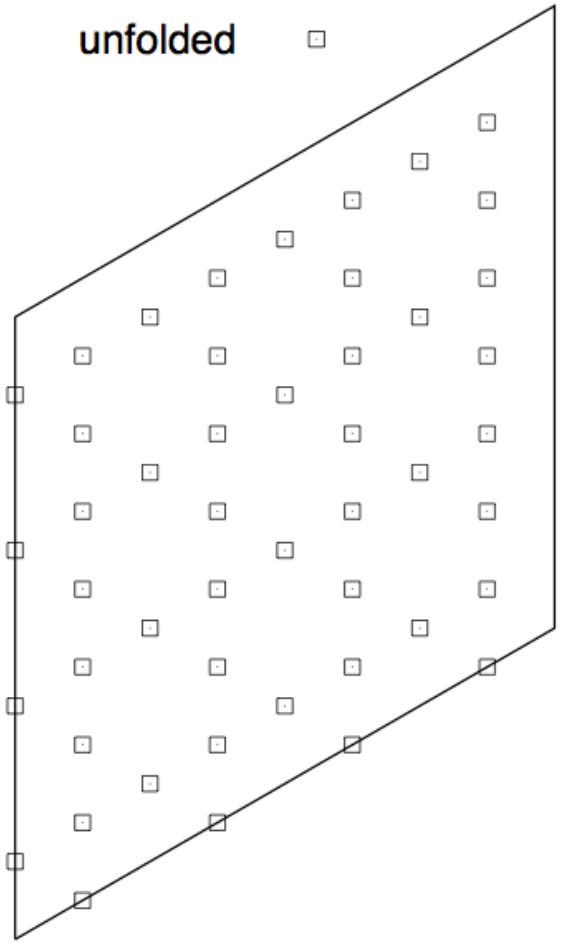
Uniform -> unfold -> shift with **q** -> reduce





(0.5, 0.5)

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



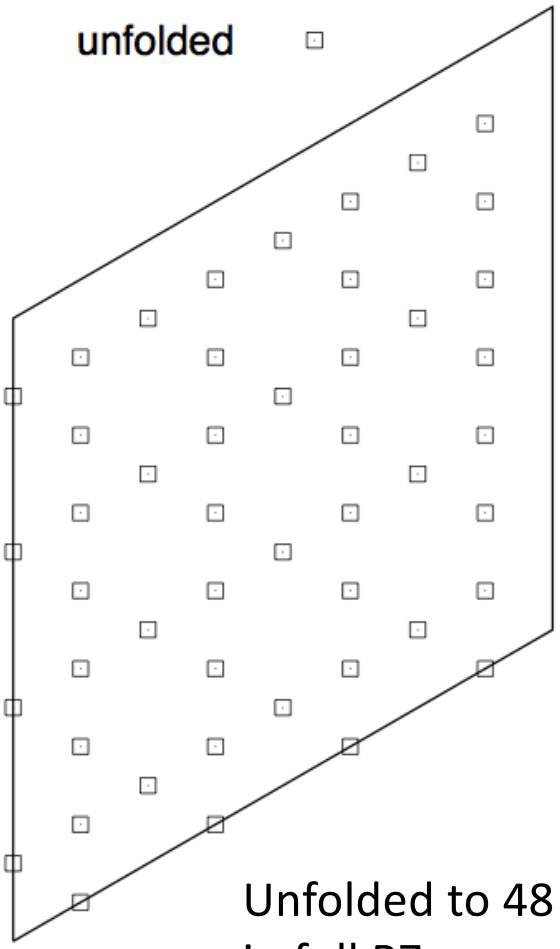
Unfolded to 48 in full BZ

Unfolding gives more points!

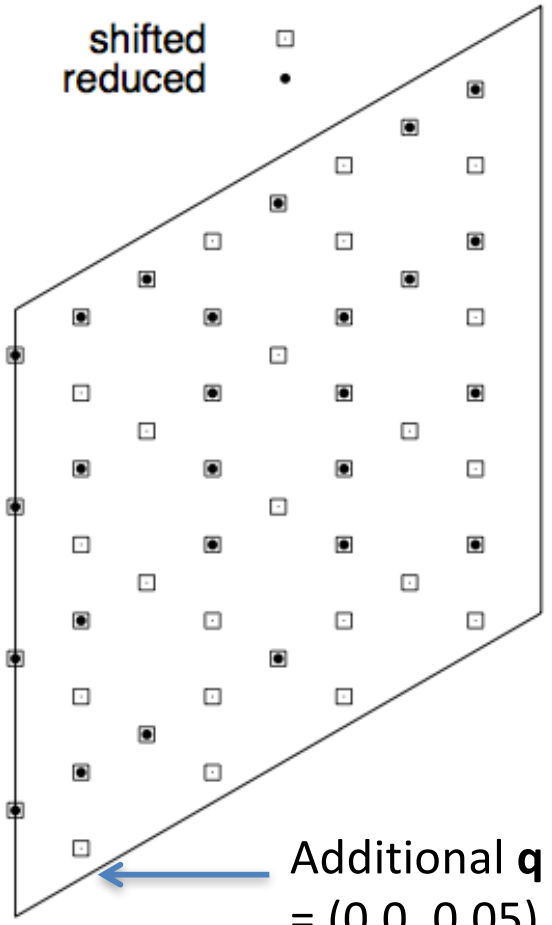
k-grid construction: 4×4 grid for graphene

`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

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

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.

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.

Solving Dyson's equation in Sigma

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

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

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

$$E_{n\mathbf{k}}^{\mathrm{QP0}} = E_{n\mathbf{k}}^{\mathrm{MF}} + \langle \psi_{n\mathbf{k}} | \Sigma(E_{n\mathbf{k}}^{\mathrm{MF}}) - \Sigma^{\mathrm{MF}} | \psi_{n\mathbf{k}} \rangle$$

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

$$E_{n\mathbf{k}}^{\mathrm{QP1}} = E_{n\mathbf{k}}^{\mathrm{QP0}} + \frac{d\Sigma_{n\mathbf{k}}/dE}{1 - d\Sigma_{n\mathbf{k}}/dE} \left(E_{n\mathbf{k}}^{\mathrm{QP0}} - E_{n\mathbf{k}}^{\mathrm{MF}} \right)$$

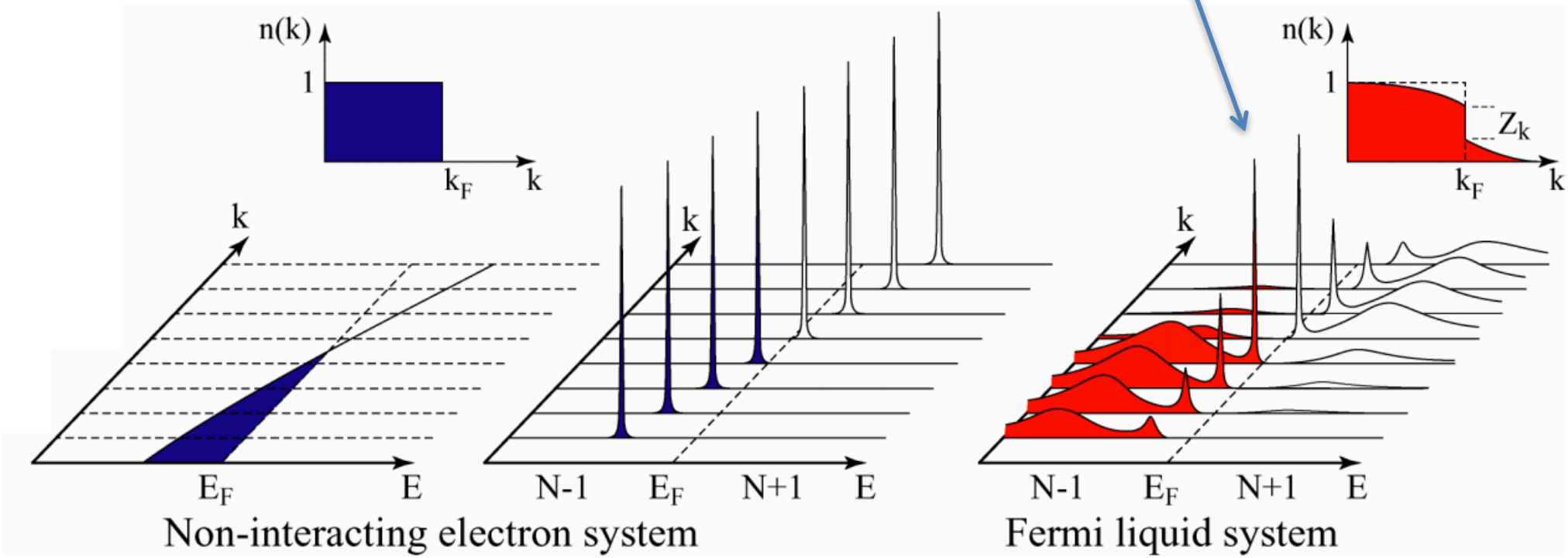
Available as columns in `sigma_hp.log`, and `eqp0.dat` and `eqp1.dat` files

Quasiparticle renormalization factor *Z*

$$E_{n\mathbf{k}}^{\mathrm{QP1}} = E_{n\mathbf{k}}^{\mathrm{QP0}} + (Z_{n\mathbf{k}} - 1)\left(E_{n\mathbf{k}}^{\mathrm{QP0}} - E_{n\mathbf{k}}^{\mathrm{MF}}\right)$$

$$Z_{n\mathbf{k}} = \frac{1}{1 - d\Sigma_{n\mathbf{k}}/dE}$$

Between 0 and 1
Weight in QP peak



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

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

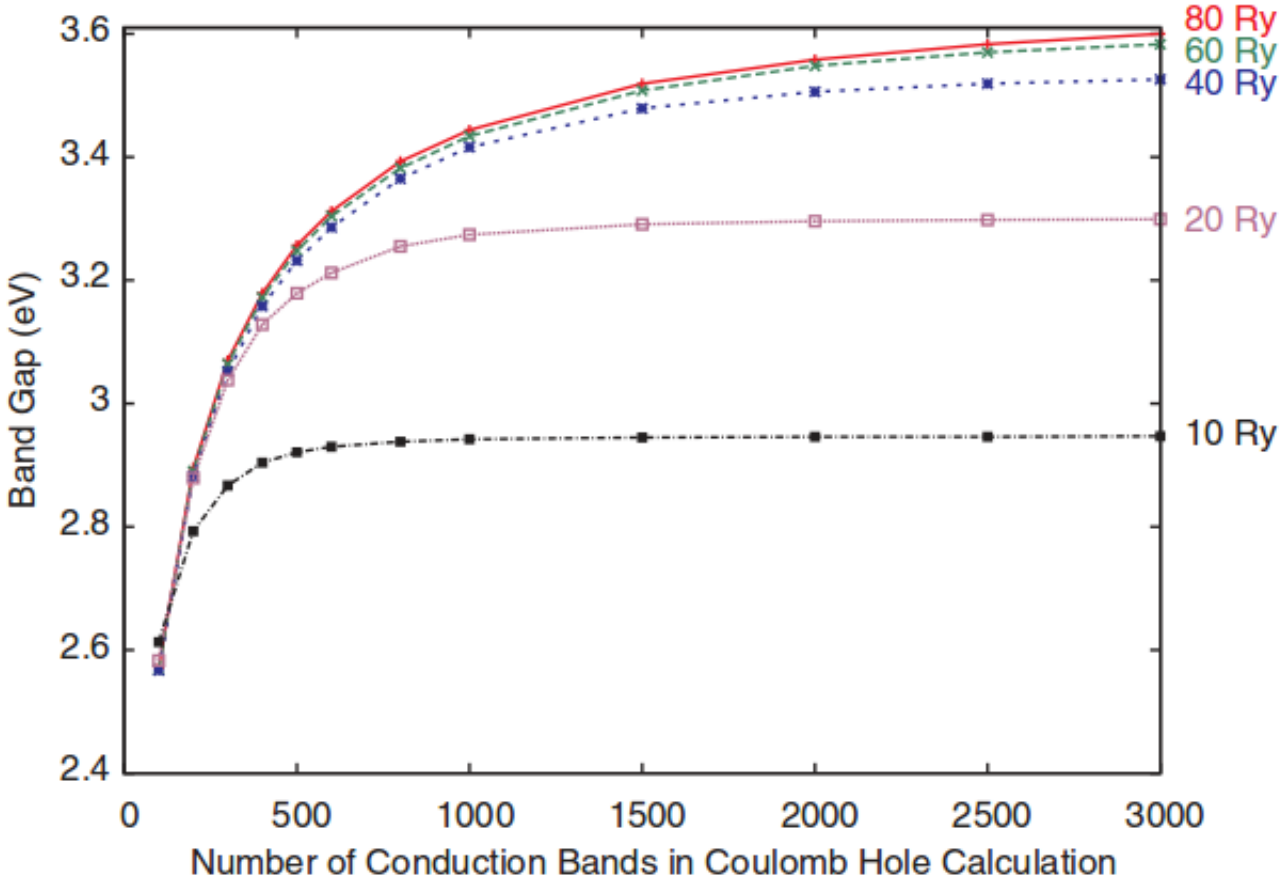
Bands in CH summation (sigma)

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

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

Wavefunction cutoff (matrix elements)

Coupled convergence parameters



B. Shih et al., ZnO

See convergence and “When things go wrong” slides on BerkeleyGW 2018 tutorial page!

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 and charged systems, unlike plane-wave codes.

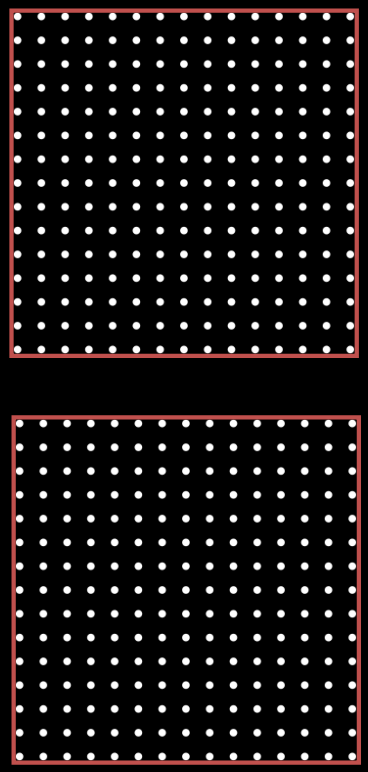
Domain parallelization for real-space scales better than plane waves.

Fourier transform to plane-wave form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G})$$

real space: cube for all quantities

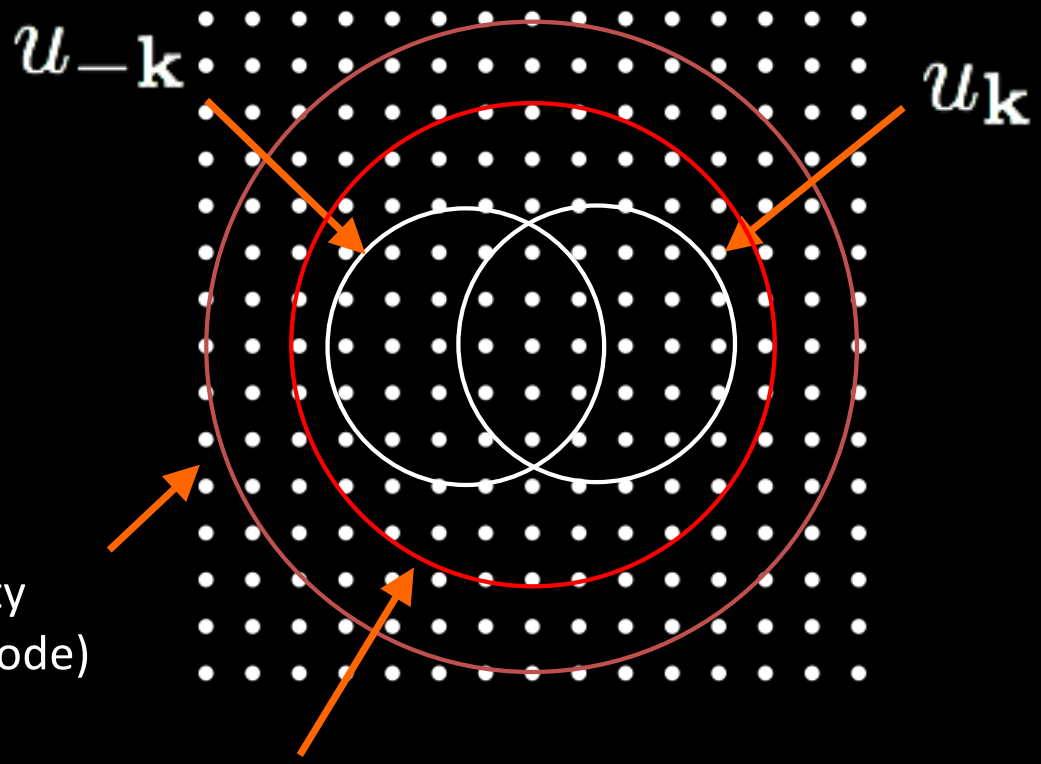
$$|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cutoff}}$$



real space

FT

reciprocal space



density (PW code)

density (real-space code)

Must check norm, renormalize.

Finite *vs.* periodic boundary conditions for vacuum

Are plane waves more natural basis for unbound vacuum states?

"Particle in a box" spectrum

$$\psi_n(x) \sim e^{in\pi x/L}$$

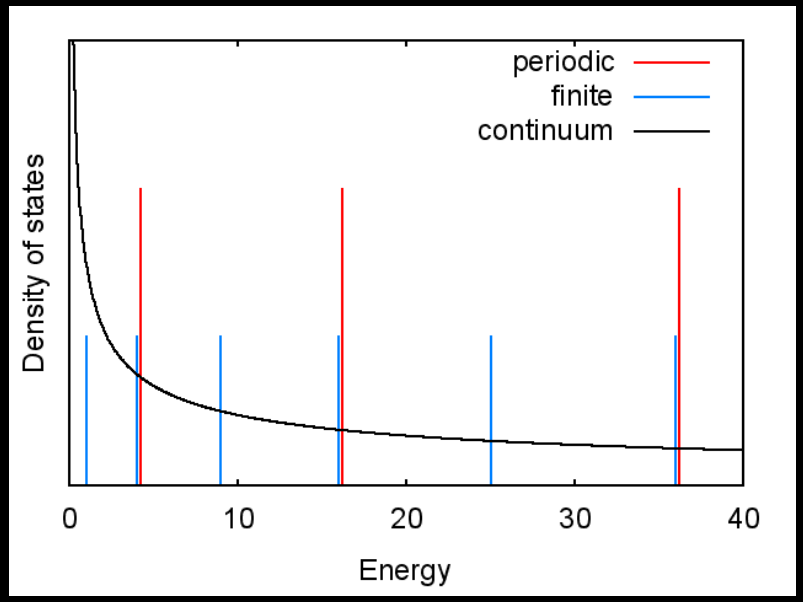
$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

periodic (plane waves) $\psi'(0) = \psi'(L) = 0$

$n = \pm 2, \pm 4, \pm 6, \ldots$

finite (real space) $\psi(0) = \psi(L) = 0$

$n = 1, 2, 3, \ldots$



The tutorial

Four examples:
(1) hexagonal boron nitride sheet
(2) benzene molecule
(3) LiCl exciton visualization
(4) silicon

Today: GW approximation
Tomorrow: Bethe-Salpeter equation

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

Calculations will be performed on Cori supercomputer at NERSC.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