Calculations of excited states of solids using BerkeleyGW

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There are three directories:

- codes: paratec (DFT); BGW
- examples: 1-MgO-GW-64-atom; 2-MgO-GW-primitive-cell; 3-GaAs-GW-BSE
- results: 1-MgO-GW-64-atom; 2-MgO-GW-primitive-cell; 3-GaAs-GW-BSE

- Please submit jobs under the examples directory; results directory contains pre-calculated results
- Since calculations of quasiparticle and electron-hole (e-h) excitations requires several steps, each example directory contains multiple sub-directories .

First example: Quasiparticle band gap of MgO

In this example, you will learn how to calculate the quasiparticle band gap (direct gap at Γ) of MgO

Directory: examples/1-MgO-GW-primitive-cell

There are three sub-directories:

- 1-paratec (DFT calculations to obtain mean-field Kohn-Sham (KS) solutions)
- 2-epsilon (Calculation of the dielectric matrix $\varepsilon_{GG'}(q)$ within the random phase approximation)
- 3-sigma (Calculation of the self-energy Σ_{nk} for selected states)

First example: Quasiparticle band gap of MgO

- First step: DFT calculations (cd 1-paratec).

  There are three sub-tasks (sub-directories):

  ✓ 1-SCF: SCF calculation

  ✓ 2-WFN: NSCF calculation to obtain KS solutions on a uniform k-grid (may or may not contain Γ point)

  ✓ 2-WFNq: NSCF calculation to obtain KS solutions on a uniform but slightly shifted k-grid from that used in WFN calculation

  Directory PSP: pseudopotentials

First example: Quasiparticle band gap of MgO

- DFT calculations sub-tasks:
  - ✓ 1-SCF: SCF calculation. There are four files under this directory which should be self-explanatory:
    - input: contain crystal structure and other control parameters
    - Mg_POT.DAT: pseudopotential file
    - O_POT.DAT: pseudopotential file
    - job.scf: job script

  Take a moment to open “input” if you want.

  All you need to do is to submit the job: sbatch job.scf

  The calculation generates a bunch of files including charge density, exchange correlation potential, etc

First example: Quasiparticle band gap of MgO

- DFT calculations sub-tasks:
  - ✓ 2-WFN: NSCF calculation to obtain KS solutions on a uniform k-grid (may or may not contain Γ point)
  - ✓ 2-WFNq: NSCF calculation to obtain KS solutions on a slightly shifted uniform k-grid

  The reason we need KS solutions on a slightly shifted k-grid has something to do with the divergence of the Coulomb potential: Coulomb potential is long-ranged and diverges as 1/q as q -> 0.

  Submit jobs: sbatch job.wfn; sbatch job.wfnq

  [More details: PRB 34, 5390 (1986); Computer Physics Communications 183, 1269 (2012)]

First example: Quasiparticle band gap of MgO

- Second step: Electron polarizability/dielectric function (cd 2-epsilon)

  Input files:

  - epsilon.inp: control file containing all parameters/options
  - WFN: wave functions on a uniform k-grid
  - Weight.dat: band integration weights [Sci. Rep. 6, 36849 (2016)]
  - WFNq: wave functions on a uniform but slightly shifted k-grid
  - job.epsilon: job script

  Take a moment to open “epsilon.inp” if you want.

  Submit job: sbatch job.epsilon. This calculation generates two files, eps0mat, epsmat, which will be used for the next step calculation.

  eps0mat: $\varepsilon_{GG'}(q \to 0)$; epsmat: $\varepsilon_{GG'}(q)$

First example: Quasiparticle band gap of MgO

- Third step: self-energy calculation (cd 3-sigma)

  Input files:

  - Sigma.inp: control file containing all parameters/options
  - RHO: charged density file (symbolic link to CD95 from SCF calculation)
  - VXC: exchange-correlation potential from SCF calculation
  - WFN_inner: wave function file
  - weight.dat: band integration weights [Sci. Rep. 6, 36849 (2016)]
  - job.epsilon: job script
  - eps0mat, epsmat: dielectric matrix from the epsilon calculation

  Take a moment to open “sigma.inp” if you want.

  Submit job: sbatch job.sigma. This calculation give the quasiparticle energy of selected states (in this case, a few states with k = 0, i.e., the Γ point)

First example: Quasiparticle band gap of MgO

- We now check the GW band gap of MgO. You can calculate the whole band structure. But for the sake of time, we will only look at the Γ point.
- The result (sigma.log):

n	elda	ecor	x	sx-x	ch	sig	vxc	eqp0	eqp1	Znk
1	-7.9775	-7.9775	-29.9993	17.4550	-10.4223	-22.9666	-18.2387	-12.7055	-11.6957	0.7864
2	9.3540	9.3540	-25.2433	14.0434	-11.8152	-23.0151	-20.1404	6.4793	6.9225	0.8458
3	9.3540	9.3540	-25.2433	14.0434	-11.8152	-23.0151	-20.1404	6.4793	6.9225	0.8458
4	9.3540	9.3540	-25.2433	14.0434	-11.8152	-23.0151	-20.1404	6.4793	6.9225	0.8458
5	14.2138	14.2138	-7.6641	4.5029	-8.3140	-11.4752	-12.0882	14.8268	14.7499	0.8745
6	25.2382	25.2382	-3.1888	1.6041	-6.2020	-7.7867	-8.9094	26.3609	26.2301	0.8835
7	25.2382	25.2382	-3.1888	1.6041	-6.2020	-7.7867	-8.9094	26.3609	26.2301	0.8835
8	25.2382	25.2382	-3.1888	1.6041	-6.2020	-7.7867	-8.9094	26.3609	26.2301	0.8835

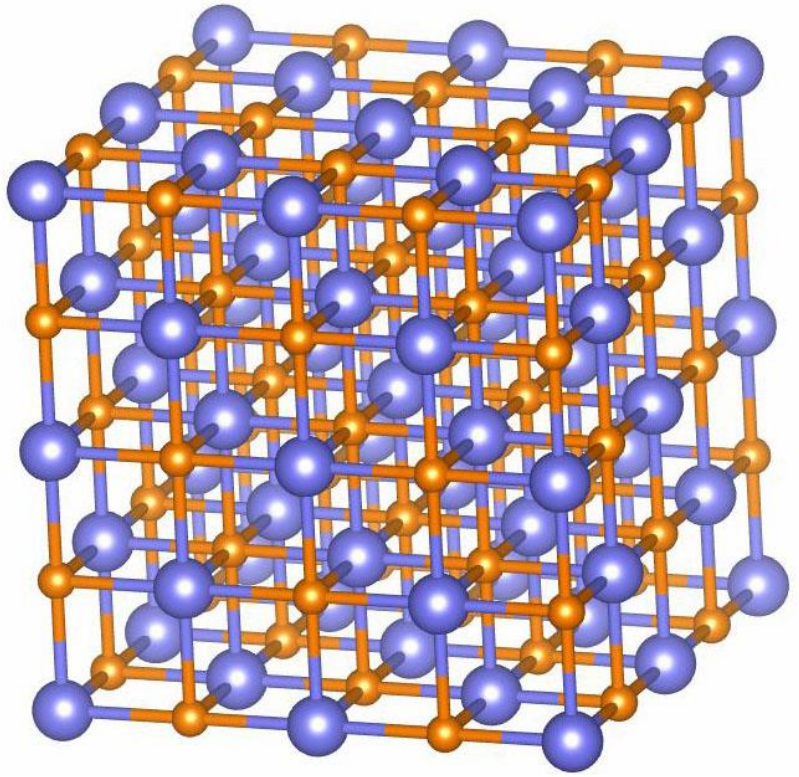
DFT-PBE band gap: 14.2138 - 9.3540 = 4.86 eV

GW band gap: 14.7499 - 6.9225 = 7.83 eV

Exp band gap: 7.78 eV

Second example: Large-scale GW calculations (a 64-atom MgO supercell)

- Computational cost of conventional GW calculations scales as $O(N^4)$ where N is the number of atoms in the system
- Conventional GW calculations are thus very expensive for large systems, and convergence is often a severe issue
- For a 2-atom MgO primitive cell, one needs to include about 1,000 bands in the GW calculations to achieve adequately converged results



- To achieve the same level of convergence for a 64-atom cell, one would need 32,000 bands! You will have to wait for a few days to get the results!

Second example: Large-scale GW calculations (a 64-atom MgO supercell)

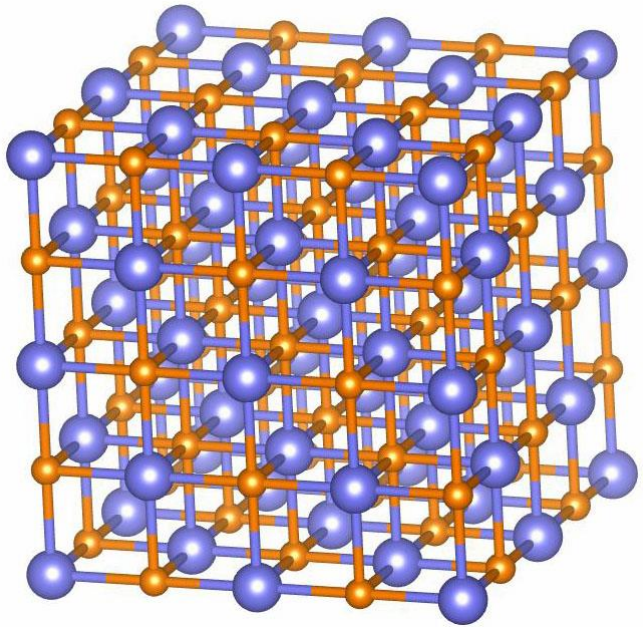
- Using our recently developed acceleration technique, a GW calculation for a 64-atom MgO takes a little over 1 hour using four 56-core (Intel Xeon Gold 6330) nodes.

- Go ahead and submit the jobs.

- In this example the WFN calculation is done slightly differently. We use a memory-saving method to generate the wave functions. So after the WFN calculation is done, please run wave functions merging script:

  ./wfnmerge.sh

Second example: Large-scale GW calculations (a 64-atom MgO supercell)



- Using our new method, we only need to carry out integration over about 920 energy points/bands
- This represents a speed up factor of 3,2000/920 ~ 35
- Results (sigma.log)

	n	elda	ecor	x	sx-x	ch	sig	vxc	eqp0	eqp1	Znk
	126	9.3525	9.3525	-25.2601	14.0797	-11.8352	-23.0156	-20.1391	6.4759	6.9192	0.8459
	127	9.3525	9.3525	-25.2601	14.0797	-11.8352	-23.0156	-20.1391	6.4759	6.9192	0.8459
VBM	128	9.3525	9.3525	-25.2601	14.0797	-11.8352	-23.0156	-20.1391	6.4759	6.9192	0.8459
CBM	129	14.2153	14.2153	-7.6819	4.5204	-8.3454	-11.5069	-12.0885	14.7969	14.7238	0.8744

DFT band gap: 4.86 eV

GW band gap: 7.80 eV (very close to that of primitive cell calculations)

Exp band gap: 7.78 eV

Third example: Exciton calculations (GW+BSE)

- The calculations of e-h excitations are more involved.
  cd 3-GaAs-GW-BSE
- There are four sub-directories:
  - ✓ 1-paratec: DFT calculations
  - ✓ 2-epsilon: Dielectric matrix calculations
  - ✓ 3-sigma: Self-energy
  - ✓ 4-BSE: Solving the Betha-Salpeter equation to obtain e-h excitations

References: PRB 62, 4927 (2000)
Computer Physics Communications 183, 1269 (2012)

Third example: Exciton calculations (GW+BSE)

- There are a few more directories under 1-paratec
  - ✓ 1-SCF
  - ✓ 2-WFN0-GW
  - ✓ 2-WFN-GW: This time we use a shifted grid for calculating $\varepsilon_{GG'}(q)$
  - ✓ 2-WFNq-GW
  - ✓ 3-WFN0-fine-grid-18-BSE
  - ✓ 3-WFN0-fine-grid-18-shifted-BSE
- Exciton calculations require an enormously dense k-grid. We use a so-called two-grid method [PRB 62, 4927 (2000); Compt. Phys. Commun. 183, 1269 (2012)].
- The e-h Kernel is first calculated on a coarse 6x6x6 k-grid, the results are then interpolated on a finer 18x18x18 grid (which is still NOT high enough!)

Third example: Exciton calculations (GW+BSE)

- After running
  - ✓ 1-SCF
  - ✓ 2-WFN0-GW
  - ✓ 2-WFN-GW
  - ✓ 2-WFNq-GW

  You may proceed to run 2-epsilon and 3-sigma

- Then cd 4-BSE/1-kernel and submit job: sbatch job.kernel (takes about 3 min)

Third example: Exciton calculations (GW+BSE)

- After running
  - ✓ 1-SCF
  - ✓ 2-WFN0-GW
  - ✓ 2-WFN-GW
  - ✓ 2-WFNq-GW

  You may proceed to run 2-epsilon and 3-sigma
- Then cd 4-BSE/1-kernel and submit job: sbatch job.kernel (takes about 3 min)
- We will use two different methods to calculate the optical absorption (imaginary part of the frequency-dependent dielectric function)
- Direction diagonalization: 4-BSE/2-exciton-absorption-k6-to-k18
- Haydock recursion method: 4-BSE/ 2-exciton-absorption-k6-to-k18-shifted-haydock

Third example: Exciton calculations (GW+BSE)

- After applying the Tamm-Dancoff approximation (TDA) which decouples the excitations and de-excitations, the BSE is reduced to a simplified eigenvalue problem (we focus on q = 0 excitons which are relevant to optical excitations)

$$(E^{QP}_{c\vec{k}} - E^{QP}_{v\vec{k}})A^{S}_{vc\vec{k}} + \sum_{v'c'\vec{k}'} <vc\vec{k}'| K^{eh} | v'c'\vec{k}'> A^{S}_{v'c'\vec{k}'} = \Omega^{S} A^{S}_{vc\vec{k}}.$$

Solving the above equation then gives the exciton wave funcion

$$\Psi^{S}(\vec{r}_e, \vec{r}_h) = \sum_{vc\vec{k}} A^{S}_{vc\vec{k}} \psi_{c\vec{k}}(\vec{r}_e) \psi^{*}_{v\vec{k}}(\vec{r}_h)$$

and related properties such as optical absorption spectra

$$\varepsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_{S} | \hat{n} \cdot < 0 | \vec{v} | S > \delta(\omega - \Omega^{S})$$

Third example: Exciton calculations (GW+BSE)

$$(E^{QP}_{c\vec{k}} - E^{QP}_{v\vec{k}})A^{S}_{vc\vec{k}} + \sum_{v'c'\vec{k}'} \langle vc\vec{k}' | K^{eh} | v'c'\vec{k}' \rangle A^{S}_{v'c'\vec{k}'} = \Omega^{S} A^{S}_{vc\vec{k}}.$$

- One can use standard eigen-solver (e.g., ScaLAPACK) to solve the BSE
- However, often it is very (sometimes prohibitively) expensive to solve the above eigenvalue problem directly, even for relatively small systems because e-h excitations calculations require an enormously dense k-grid (e.g. 60x60x60 or higher).
- The dimension of the matrix: $N_k \times N_v \times N_c$
- For example, it takes about 80 mins to diagonalize the above equation for GaAs using 224 cores ($N_k = 18 \times 18 \times 18 = 5832;\ N_v = 3;\ N_c = 4$)
- The matrix size is ~ 70,000 x 70,000!
- Direction diagonalization directory: 4-BSE/2-exciton-absorption-k6-to-k18

Third example: Exciton calculations (GW+BSE)

$$(E^{QP}_{c\vec{k}} - E^{QP}_{v\vec{k}})A^{S}_{vc\vec{k}} + \sum_{v'c'\vec{k}'} <vc\vec{k}'|\, K^{eh}\, |v'c'\vec{k}'> A^{S}_{v'c'\vec{k}'} = \Omega^{S} A^{S}_{vc\vec{k}}.$$

- Direction diagonalization directory: 4-BSE/2-exciton-absorption-k6-to-k18
- With direct diagonalization, you get all eigenvalues and eigenvectors
- This is useful if you need to analyze the excitonic wave functions and the details of the excitonic states (e.g., exciton binding energy)

- Haydock recursion method: 4-BSE/2-exciton-absorption-k6-to-k18-shifted-haydock
- Advantages: Fast, gives optical absorption directly
- Disadvantages: Cannot give eigenvalues and eigenvectors

Haydock recursion method: PRB 59, 5441 (1999)

Interacting vs non-interacting optical absorption

- We use a two-grid method to reduce the computational cost
- Coarse k-grid: 6x6x6
- Fine k-grid: 18x18x18 (shifted)
- Numbers of valence and conduction bands: Nv=3; Nc=4
- Haydock recursion method to obtain the optical absorption
- Absorption spectra data:
  absorption_eh.dat
  absorption_neh.dat
- Not converged!