JDFT + RPA + GW calculations in practice with JDFTx + BGW

3rd Annual BEAST Workshop

Jacob Clary

August 23, 2024

U.S. DEPARTMENT OF ENERGY
Office of Science
Award # DE-SC0022247

Moving beyond DFT: calculating RPA energies

- Replace DFT exchange-correlation energy with exact exchange energy and RPA correlation energy

$$E_{RPA} = E_{DFT} - E_{XC} + E_{XX} + E_{corr,RPA}$$

- How do we calculate each energy component?
  - JDFTx → E_{DFT}, E_{XC}, E_{XX}
  - BerkeleyGW → $E_{corr,RPA}$

- Steep scaling for RPA correlation energy
  - BerkeleyGW can scale to thousands of atoms

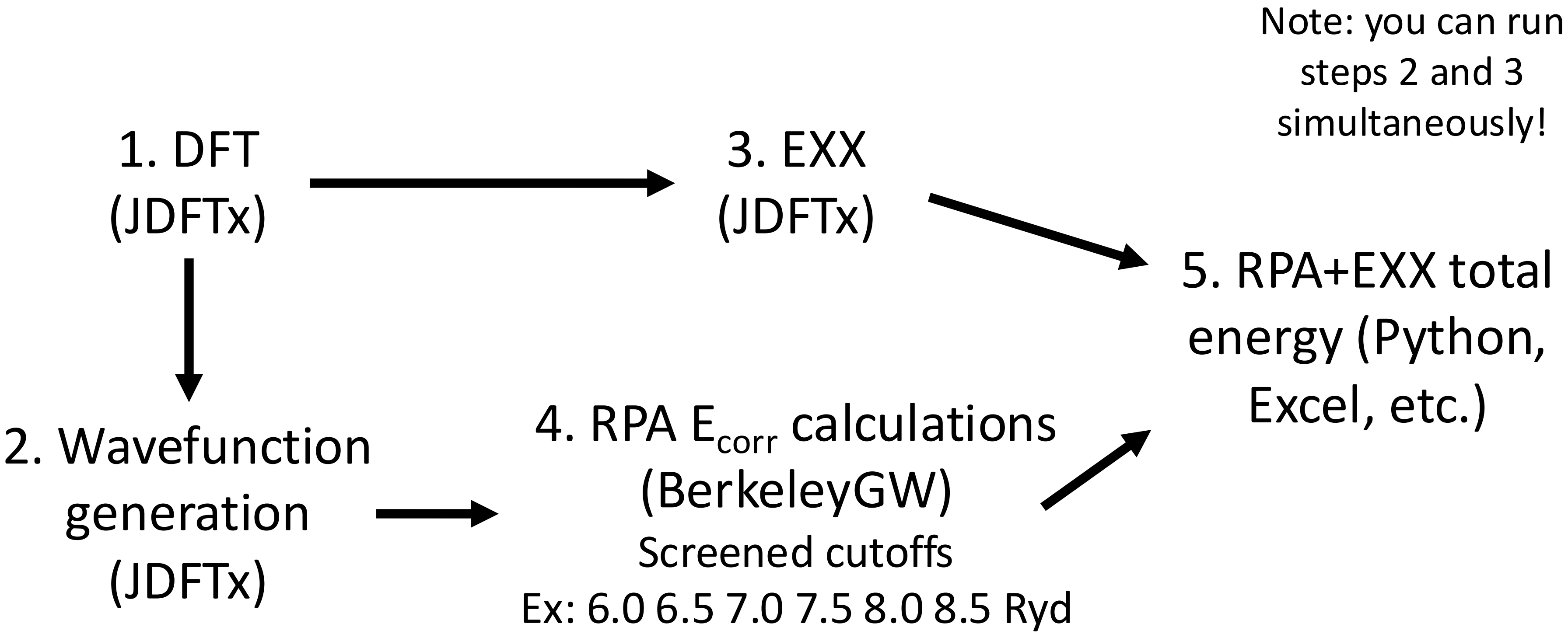
Moving beyond DFT: calculating GW electronic structures

- GW electronic structure “compatible” with RPA total energies
  - The RPA is used for χ^0, which is used to calculate correlation E
  - GW uses χ^0 within the RPA to (eventually) calculate the self-energy, Σ
- Update the DFT eigenvalues with GW quasiparticle (QP) eigenvalues
  - Either single shot (G_0W_0) or self-consistent QP eigenvalues (GW_0)

- How do we calculate these new eigenvalues?
  - JDFTx → ε_{nk}^{DFT}
  - BerkeleyGW → ε_{nk}^{GW}

- Steep scaling for GW electronic structures
  - BerkeleyGW can scale to thousands of atoms

Practical workflow for RPA total energies



Note: you can run steps 2 and 3 simultaneously!

1. DFT (JDFTx)

3. EXX (JDFTx)

5. RPA+EXX total energy (Python, Excel, etc.)

2. Wavefunction generation (JDFTx)

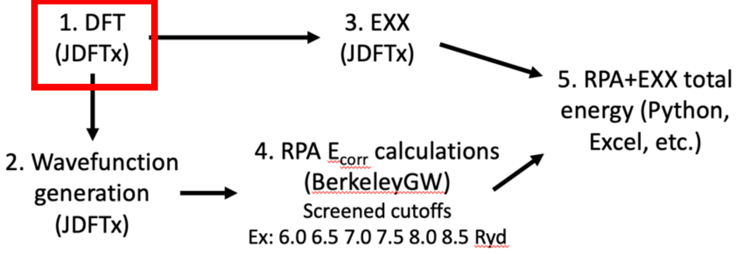
4. RPA E_{corr} calculations (BerkeleyGW)

Screened cutoffs

Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

- Both GW and RPA require many unoccupied states to be converged, this is done in step 2 of the workflow
- This assumes you will be studying a metallic system
- If you want to study gapped materials, you will need to have special adjustments to the q-point grid, see the BerkeleyGW docs about this

1. Standard DFT calculation with JDFTx



1. DFT (JDFTx)

2. Wavefunction generation (JDFTx)

3. EXX (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)
Screened cutoffs
Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

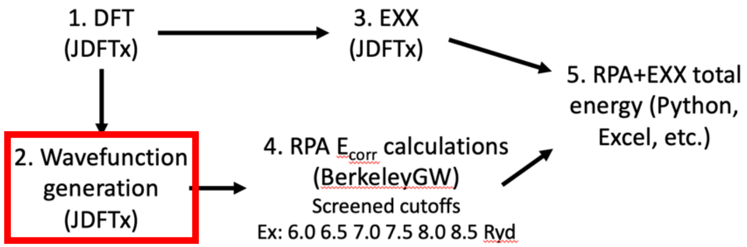
5. RPA+EXX total energy (Python, Excel, etc.)

- See tutorials from yesterday for inputs
  - Standard DFT calculation

- Pay attention to convergence
  - RPA and EXX calculations may converge slower with respect to planewave cutoff and k-grid density than DFT calculations

- Keep in mind the RPA cost scales quickly with number of electrons and size of supercell, so you should carefully think about what exactly you want to study before starting the workflow!

2. Empty state generation with JDFTx


1. DFT (JDFTx)

2. Wavefunction generation (JDFTx)

3. EXX (JDFTx)

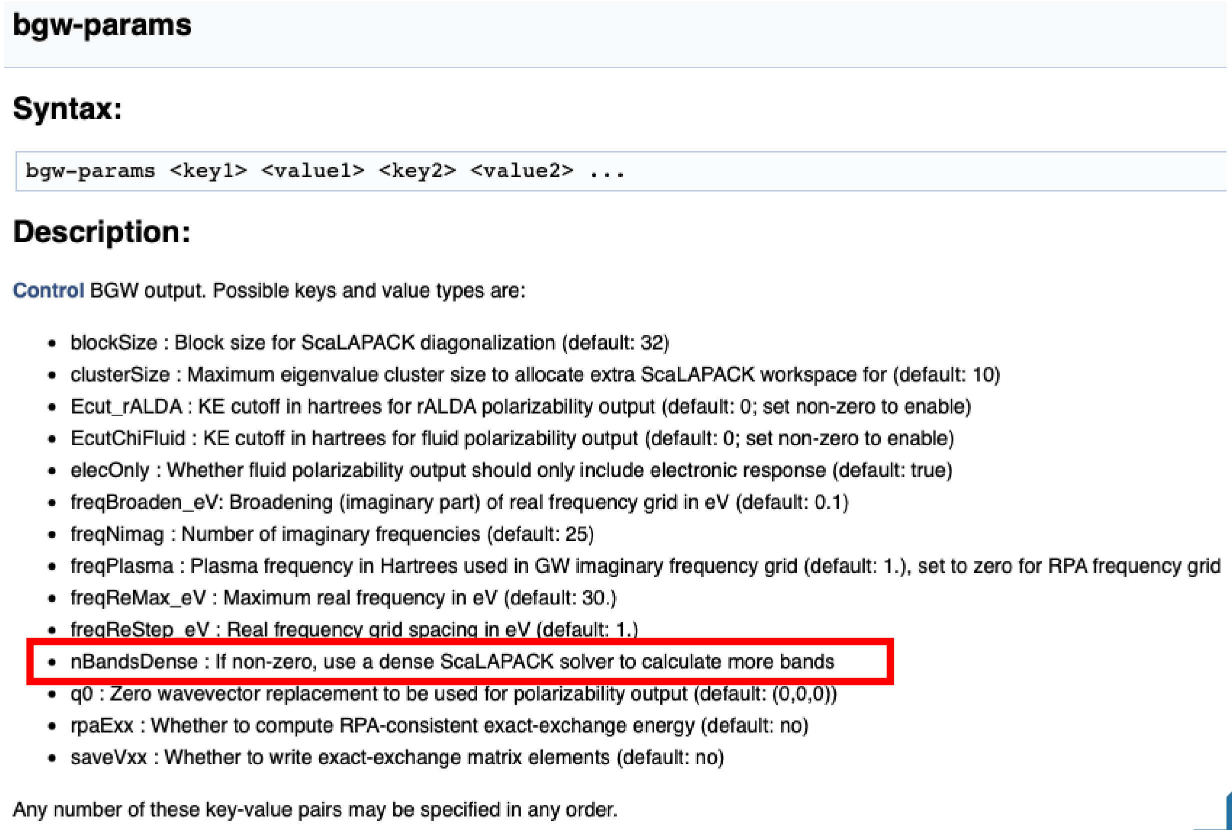
4. RPA E_{corr} calculations (BerkeleyGW)

Screened cutoffs

Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

5. RPA+EXX total energy (Python, Excel, etc.)

- JDFTx can produce output for BerkeleyGW to read later
  - bgw-params


bgw-params

Syntax:

```
bgw-params <key1> <value1> <key2> <value2> ...
```

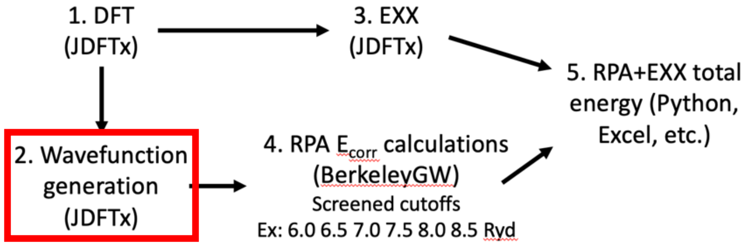
Description:

Control BGW output. Possible keys and value types are:

- blockSize : Block size for ScaLAPACK diagonalization (default: 32)
- clusterSize : Maximum eigenvalue cluster size to allocate extra ScaLAPACK workspace for (default: 10)
- Ecut_rALDA : KE cutoff in hartrees for rALDA polarizability output (default: 0; set non-zero to enable)
- EcutChiFluid : KE cutoff in hartrees for fluid polarizability output (default: 0; set non-zero to enable)
- elecOnly : Whether fluid polarizability output should only include electronic response (default: true)
- freqBroaden_eV: Broadening (imaginary part) of real frequency grid in eV (default: 0.1)
- freqNimag : Number of imaginary frequencies (default: 25)
- freqPlasma : Plasma frequency in Hartrees used in GW imaginary frequency grid (default: 1.), set to zero for RPA frequency grid
- freqReMax_eV : Maximum real frequency in eV (default: 30.)
- freqReStep_eV : Real frequency grid spacing in eV (default: 1.)
- nBandsDense : If non-zero, use a dense ScaLAPACK solver to calculate more bands
- q0 : Zero wavevector replacement to be used for polarizability output (default: (0,0,0))
- rpaExx : Whether to compute RPA-consistent exact-exchange energy (default: no)
- saveVxx : Whether to write exact-exchange matrix elements (default: no)

Any number of these key-value pairs may be specified in any order.

2. Empty state generation with JDFTx



1. DFT (JDFTx)

2. Wavefunction generation (JDFTx)

3. EXX (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)
Screened cutoffs
Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

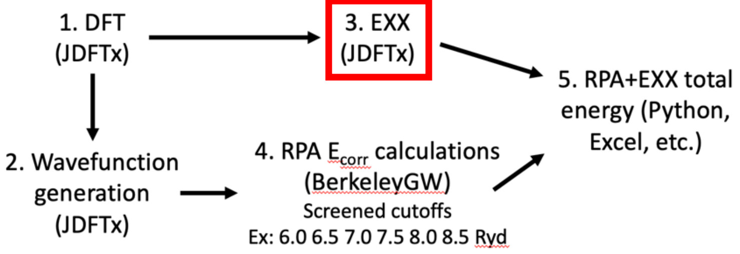
5. RPA+EXX total energy (Python, Excel, etc.)

New tags appended to ”in” file

```
fix-electron-density jdft.$VAR
bgw-params nBandsDense 500 blockSize 96
dump End BGW
```

- Perform fixed electron density calculation starting from converged DFT calculation
- The bgw-params tag tells JDFTx to use SCALAPACK to do a dense diagonalization and generate 500 bands in the wfn
  - The dump command tells JDFTx to print jdft.bgw.wfn.h5
- Use same k-point settings as 1-scf job
- These wavefunctions can be huge! ~1 – 500 GB

3. Exact exchange calculation w/ JDFTx



1. DFT (JDFTx)

3. EXX (JDFTx)

5. RPA+EXX total energy (Python, Excel, etc.)

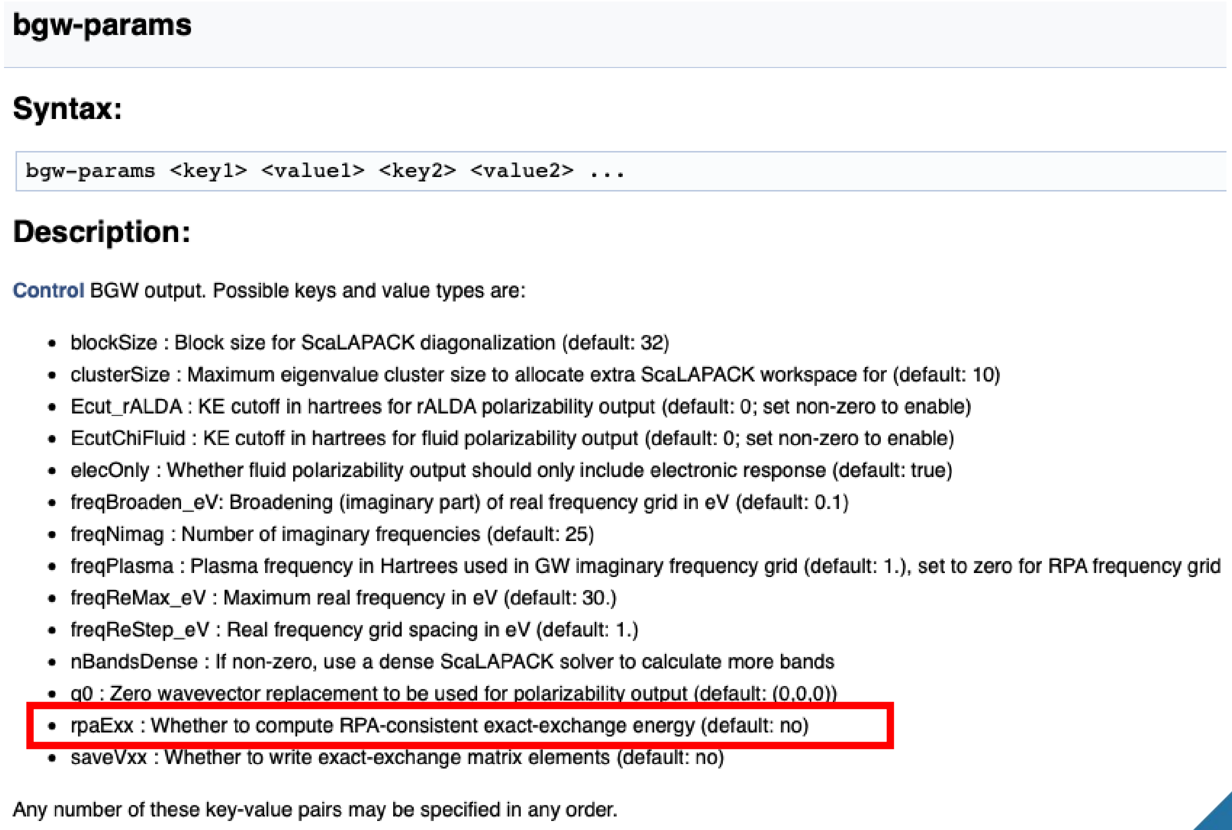
2. Wavefunction generation (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)

Screened cutoffs

Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

- Since this is a calculation for the RPA workflow, use the same tag as for step 2
  - bgw-params



bgw-params

Syntax:

```
bgw-params <key1> <value1> <key2> <value2> ...
```

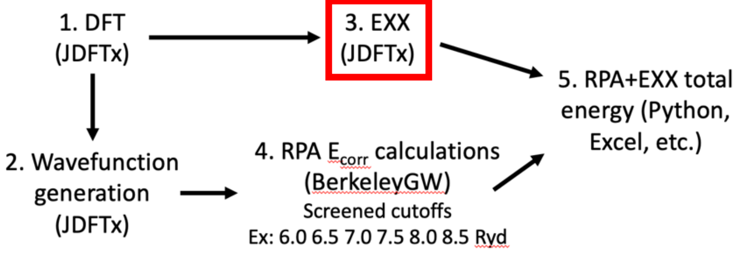
Description:

Control BGW output. Possible keys and value types are:

- blockSize : Block size for ScaLAPACK diagonalization (default: 32)
- clusterSize : Maximum eigenvalue cluster size to allocate extra ScaLAPACK workspace for (default: 10)
- Ecut_rALDA : KE cutoff in hartrees for rALDA polarizability output (default: 0; set non-zero to enable)
- EcutChiFluid : KE cutoff in hartrees for fluid polarizability output (default: 0; set non-zero to enable)
- elecOnly : Whether fluid polarizability output should only include electronic response (default: true)
- freqBroaden_eV: Broadening (imaginary part) of real frequency grid in eV (default: 0.1)
- freqNimag : Number of imaginary frequencies (default: 25)
- freqPlasma : Plasma frequency in Hartrees used in GW imaginary frequency grid (default: 1.), set to zero for RPA frequency grid
- freqReMax_eV : Maximum real frequency in eV (default: 30.)
- freqReStep_eV : Real frequency grid spacing in eV (default: 1.)
- nBandsDense : If non-zero, use a dense ScaLAPACK solver to calculate more bands
- q0 : Zero wavevector replacement to be used for polarizability output (default: (0,0,0))
- rpaExx : Whether to compute RPA-consistent exact-exchange energy (default: no)
- saveVxx : Whether to write exact-exchange matrix elements (default: no)

Any number of these key-value pairs may be specified in any order.

3. Exact exchange calculation w/ JDFTx



1. DFT (JDFTx)

3. EXX (JDFTx)

5. RPA+EXX total energy (Python, Excel, etc.)

2. Wavefunction generation (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)

Screened cutoffs

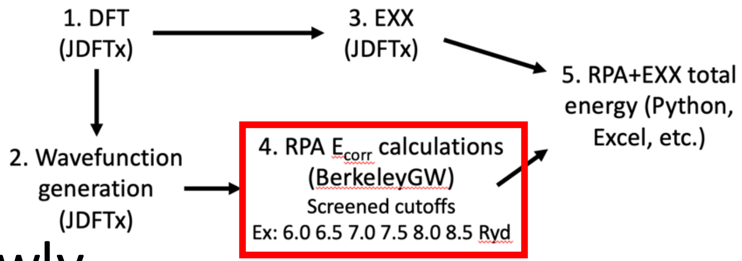
Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

New tags appended to ”in” file

```
fix-electron-density jdft.$VAR
bgw-params rpaExx yes
```

- Perform fixed electron density calculation starting from converged DFT calculation
- The bgw-params tag tells JDFTx to calculate EXX energy
- Use same k-point settings as 1-scf job

4. RPA correlation energy with BGW



1. DFT (JDFTx)

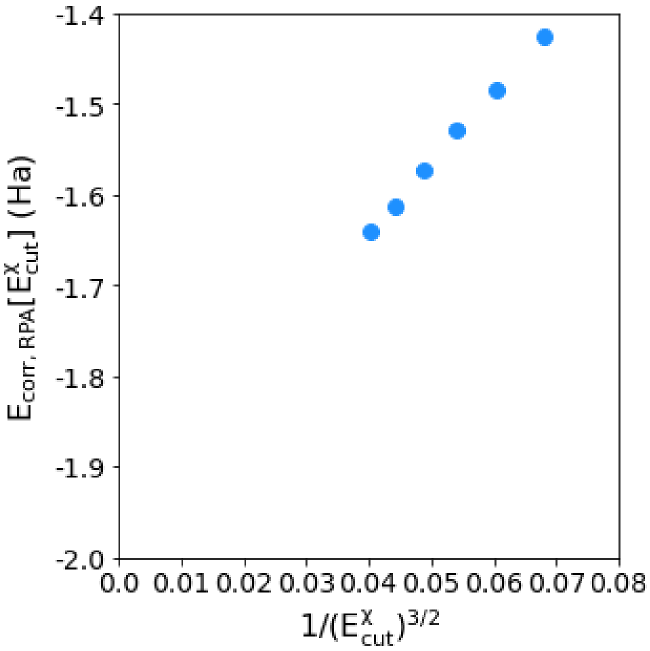
2. Wavefunction generation (JDFTx)

3. EXX (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)
Screened cutoffs
Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

5. RPA+EXX total energy (Python, Excel, etc.)

- RPA correlation energies converge slowly with respect to screened cutoff
  - Extrapolate to infinite screened cutoff
  - Each calculation is individually expensive
- The screened cutoff/number of bands change together
  - Screened cutoff defines max cutoff for G-vectors used for χ



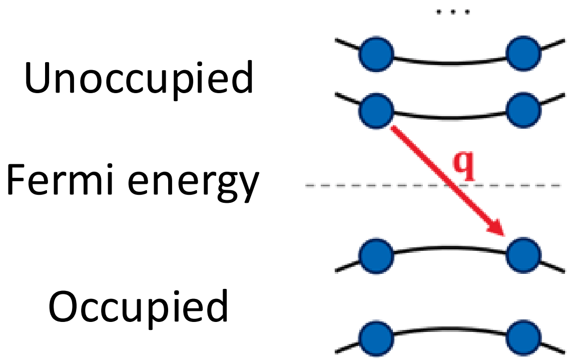
epsilon.inp key tags

cell_slab_truncation
epsilon_cutoff 6.0
number_bands 166
nbasis_subspace 166
number_core_excluded 12

Set same as DFT E_F and broadening

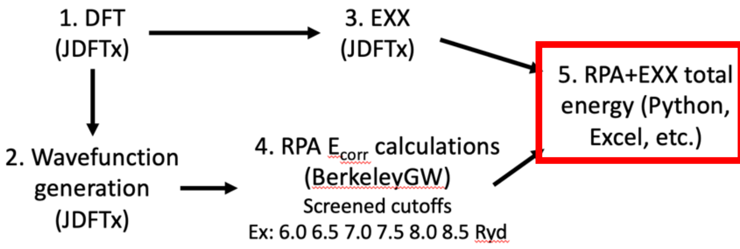
fermi_level 7.5542
fermi_level_absolute
occ_broadening 0.2721

Note about k/q-grids in BGW



- BGW needs an explicit list of k/q-points
  - Convergence is usually best for RPA+EXX and GW if all calculations use same grid
  - See BGW docs for detailed syntax
  - Polarizability and dielectric matrices calculated on q-point grid
    - Regular, Γ-centered grid obtained from all transfer vectors $q = k' - k$
  - “dump End Kpoints” tells JDFTx to print the irreducible k-points it finds
    - These points should be copied into BGW epsilon/sigma input files
  - "kpoint-reduce-inversion no” is needed because BGW never uses time-reversal symmetry
- For metals (as in the Pt+H adsorption tutorial here), we neglect the long-wave contribution and replace q → 0 with the next smallest magnitude q-point
  - https://doi.org/10.1103/PhysRevB.81.115126

5. Extrapolation of RPA energies



1. DFT (JDFTx)

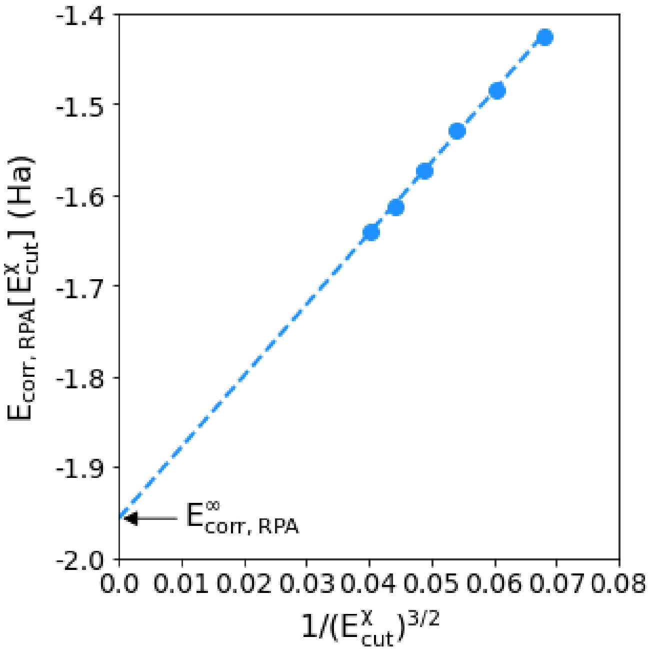
2. Wavefunction generation (JDFTx)

3. EXX (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)
Screened cutoffs
Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

5. RPA+EXX total energy (Python, Excel, etc.)

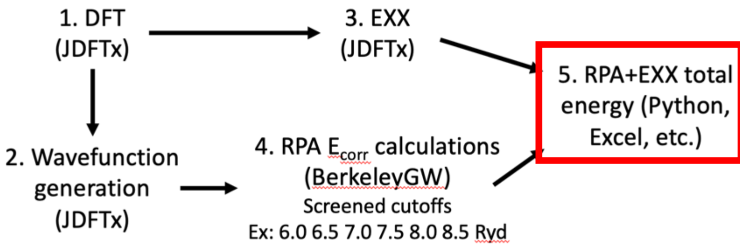
- Can be done with any post-processing analysis tool
  - Python, Excel, MATLAB, etc.
- Extrapolate to infinite screened cutoff (y-axis)
  - 5-8 points for extrapolation is common, depending on size and fit of extrapolation
- Assumes electrons behave as free-electron gas



Arbitrary fitted coefficient

$$E_{corr,RPA}\left[E_{cut}^{\chi}\right] = E_{corr,RPA}^{\infty} + \frac{A}{\left(E_{cut}^{\chi}\right)^{\frac{3}{2}}}$$

6. RPA total energy calculation



1. DFT (JDFTx)

2. Wavefunction generation (JDFTx)

3. EXX (JDFTx)

4. RPA E_{corr} calculations (BerkeleyGW)
Screened cutoffs
Ex: 6.0 6.5 7.0 7.5 8.0 8.5 Ryd

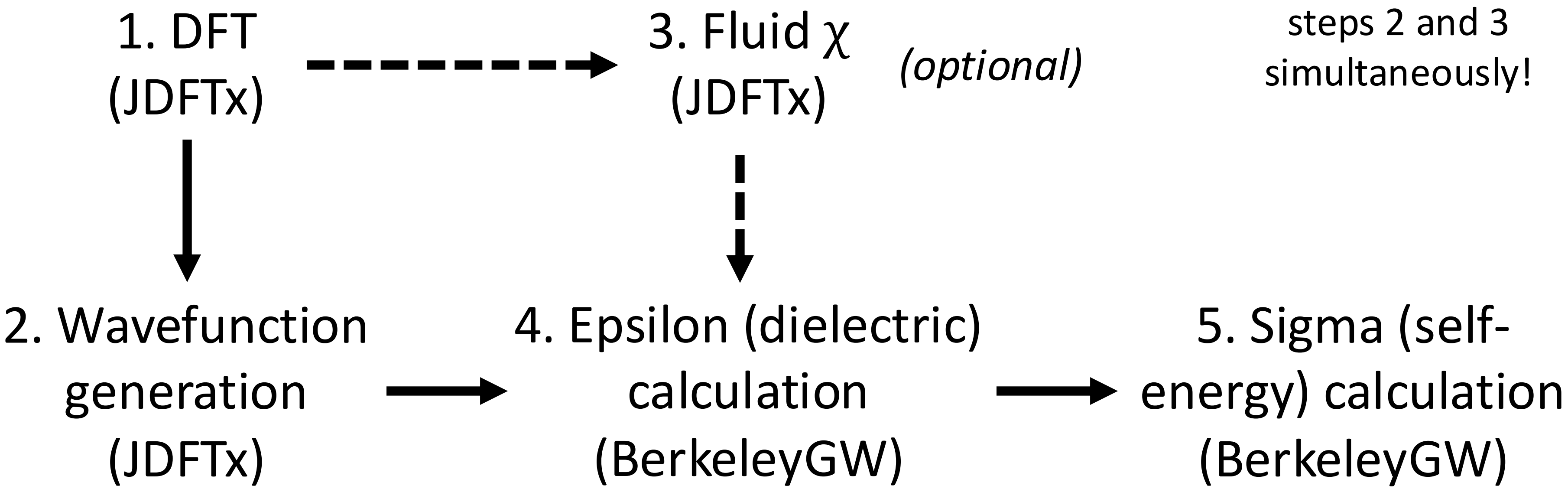
5. RPA+EXX total energy (Python, Excel, etc.)

$$E_{RPA} = E_{DFT} - E_{XC} + E_{XX} + E_{corr,RPA}$$

- Find each energy component from the ends of the JDFTx/BGW out files
  - JDFTx DFT calculation → E_{DFT}, E_{XC}
  - JDFTx EXX calculation → E_{XX}
  - BerkeleyGW → $E_{corr,RPA}$

- Repeat this entire process for each system needed to calculate an adsorption energy

Practical workflow for GW electronic structures



1. DFT (JDFTx)

3. Fluid χ (JDFTx)

(optional)

2. Wavefunction generation (JDFTx)

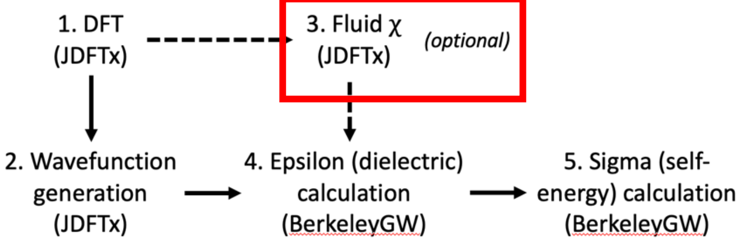
4. Epsilon (dielectric) calculation (BerkeleyGW)

5. Sigma (self-energy) calculation (BerkeleyGW)

Note: you can run steps 2 and 3 simultaneously!

- Steps 1 and 2 are the same as for RPA
- Both GW and RPA require many unoccupied states to be converged (step 2)
- This assumes you will be studying a metallic system
- If you want to study gapped materials, you will need to have special adjustments to the q-point grid, see the BerkeleyGW docs about this
- To compare vacuum to solvated jobs, need to have 2 separate workflows because starting from different DFT wavefunctions

3. Fluid χ generation with JDFTx



1. DFT (JDFTx)

3. Fluid χ (JDFTx) *(optional)*

2. Wavefunction generation (JDFTx)

4. Epsilon (dielectric) calculation (BerkeleyGW)

5. Sigma (self-energy) calculation (BerkeleyGW)

- See tutorial on solvated GW calculations

- Adjusts the screening environment of the surface

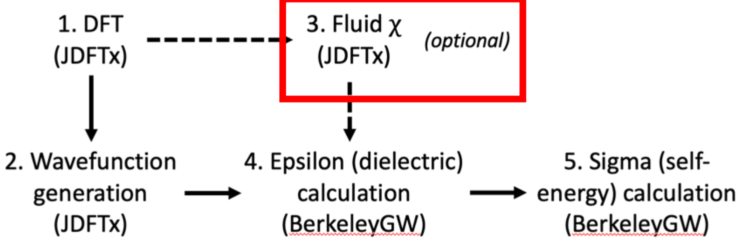
- Uses the bgw-params JDFTx input tag to output file containing the fluid polarizability

- File is read by BGW and incorporated into the GW calculation
  - RPA still in development

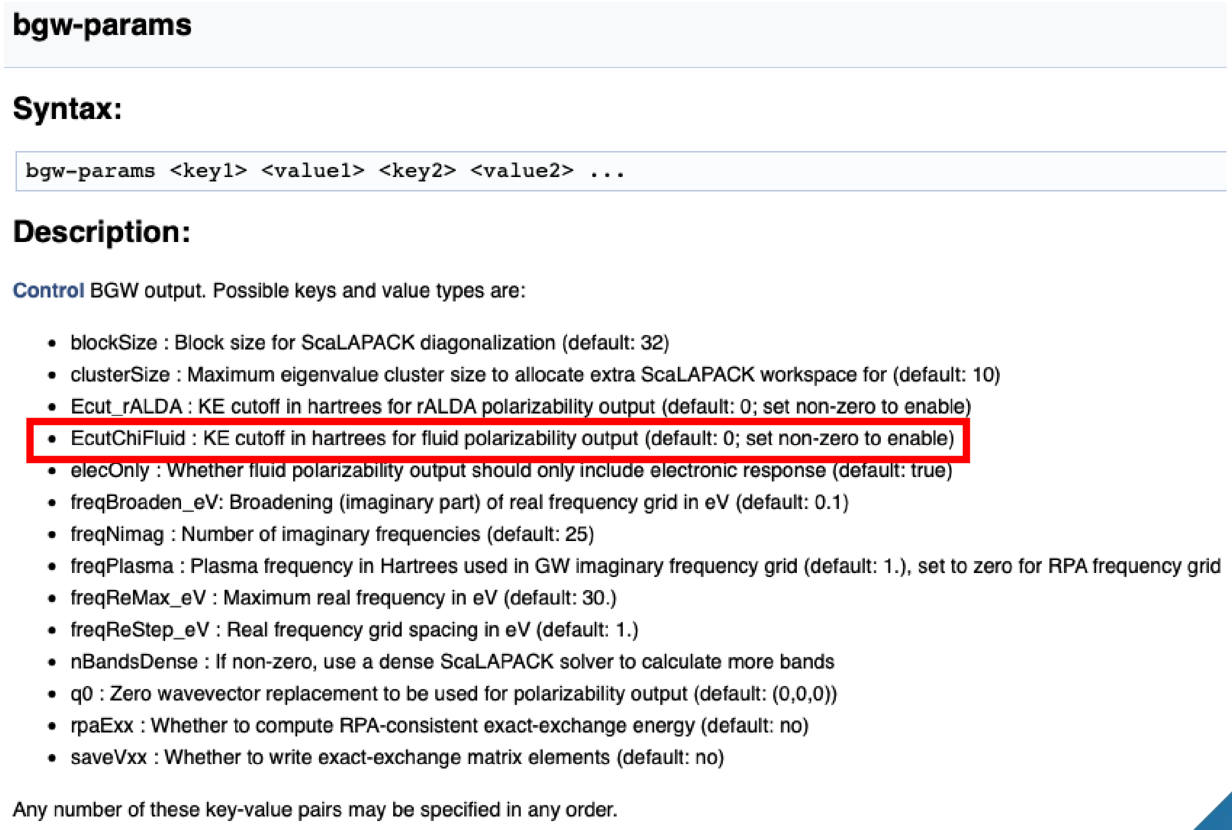
- Must generate a separate fluid χ file for each screened cutoff used in the GW calculations when testing convergence
  - Note that they can be large (100s GB to TB)!

- Resulting file allows both solvated wavefunctions AND fluid screening to impact beyond-DFT results

3. Fluid χ generation with JDFTx


1. DFT (JDFTx)
3. Fluid χ (JDFTx)
(optional)
2. Wavefunction generation (JDFTx)
4. Epsilon (dielectric) calculation (BerkeleyGW)
5. Sigma (self-energy) calculation (BerkeleyGW)

- JDFTx can produce output for BerkeleyGW to read later
  - bgw-params



bgw-params

Syntax:

```
bgw-params <key1> <value1> <key2> <value2> ...
```

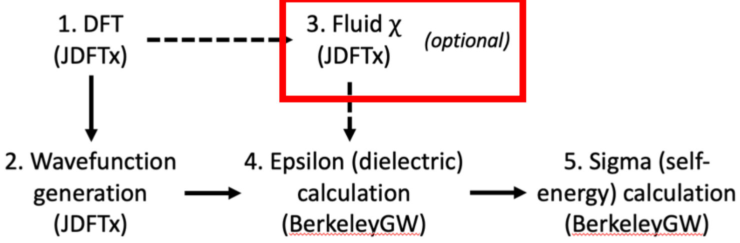
Description:

Control BGW output. Possible keys and value types are:

- blockSize : Block size for ScaLAPACK diagonalization (default: 32)
- clusterSize : Maximum eigenvalue cluster size to allocate extra ScaLAPACK workspace for (default: 10)
- Ecut_rALDA : KE cutoff in hartrees for rALDA polarizability output (default: 0; set non-zero to enable)
- EcutChiFluid : KE cutoff in hartrees for fluid polarizability output (default: 0; set non-zero to enable)
- elecOnly : Whether fluid polarizability output should only include electronic response (default: true)
- freqBroaden_eV: Broadening (imaginary part) of real frequency grid in eV (default: 0.1)
- freqNimag : Number of imaginary frequencies (default: 25)
- freqPlasma : Plasma frequency in Hartrees used in GW imaginary frequency grid (default: 1.), set to zero for RPA frequency grid
- freqReMax_eV : Maximum real frequency in eV (default: 30.)
- freqReStep_eV : Real frequency grid spacing in eV (default: 1.)
- nBandsDense : If non-zero, use a dense ScaLAPACK solver to calculate more bands
- q0 : Zero wavevector replacement to be used for polarizability output (default: (0,0,0))
- rpaExx : Whether to compute RPA-consistent exact-exchange energy (default: no)
- saveVxx : Whether to write exact-exchange matrix elements (default: no)

Any number of these key-value pairs may be specified in any order.

3. Fluid χ generation with JDFTx



1. DFT (JDFTx)

3. Fluid χ (JDFTx) *(optional)*

2. Wavefunction generation (JDFTx)

4. Epsilon (dielectric) calculation (BerkeleyGW)

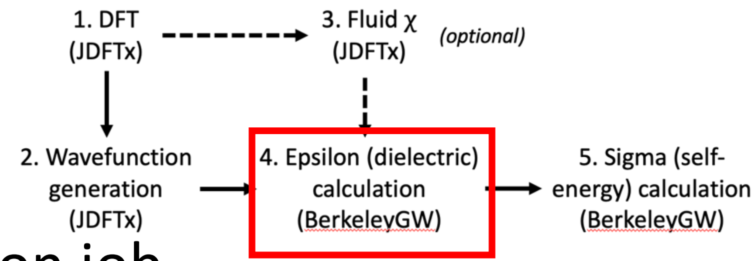
5. Sigma (self-energy) calculation (BerkeleyGW)

New tags appended to ”in” file

```
fix-electron-density jdft.$VAR
bgw-params EcutChiFluid 2.5 freqReMax_eV 20.0 freqNimag 15 freqReStep_eV 0.25
```

- Perform fixed electron density calculation starting from converged DFT calculation
- SaLSA is currently only implicit solvation model compatible
- The bgw-params tag tells JDFTx to write the fluid polarizability (chi) file. EcutChiFluid is the same as the screened cutoff in epsilon.inp but in Ha instead of Ryd
- The frequency parameters used here must match those used in epsilon.inp
- Use same k-point settings as 1-scf job

4. GW epsilon calculation


1. DFT (JDFTx)
3. Fluid χ (JDFTx)
(optional)
2. Wavefunction generation (JDFTx)
4. Epsilon (dielectric) calculation (BerkeleyGW)
5. Sigma (self-energy) calculation (BerkeleyGW)

- Generally similar tags as for RPA epsilon job
- If present, fluid polarizability file(s) is (are) read here and used to modify electronic polarizability
  - There will be 1 file for q_0 and another for the rest of the q-points
- Writes epsilon matrix file(s) that will be read by sigma code in next step
- Recommend looking at BGW docs

epsilon.inp new key tags

Match those on previous slide. Affect convergence of calculation

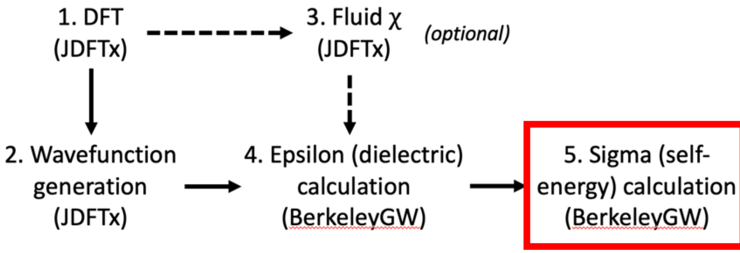
delta_frequency 0.25
frequency_low_cutoff 20.0
number_imaginary_freqs 15
broadening 0.1

Read fluid polarizability

read_chi_add
chi_eigenvalue_cutoff 1.0E-6

Note: k/q-point slide from the RPA section applies to this workflow as well

5. GW sigma calculation


1. DFT (JDFTx)
3. Fluid χ (JDFTx)
(optional)
2. Wavefunction generation (JDFTx)
4. Epsilon (dielectric) calculation (BerkeleyGW)
5. Sigma (self-energy) calculation (BerkeleyGW)

- Generally similar tags as for epsilon
- GW convergence is non-trivial and important to consider
- Reads epsilon matrix file from last step to calculate self-energy and quasiparticle eigenvalues, these can be plotted for a GW electronic structure
- eqp1.dat is file with eigenvalues you should use (DFT and GW eigenvalues together)
- Recommend looking at BGW docs

	sigma.inp new key tags
Generally match these cutoffs/bands to epsilon.inp	screened_coulomb_cutoff 5.0
	number_bands 500
Specify bands for which you want GW eigenvalues. Smaller range = much cheaper job	band_index_min 2
	band_index_max 16

Note about convergence

- The convergence of GW/RPA is non-trivial!
  - Much more involved than DFT calculations usually
- See the BerkeleyGW tutorials for more resources for GW convergence
  - Screened cutoff, epsilon number of bands, sigma number of bands crucial
- RPA convergence has been studied in these papers in these papers for example
  - Assessing the quality of the random phase approximation for lattice constants and atomization energies of solids, https://journals.aps.org/prb/abstract/10.1103/PhysRevB.81.115126
  - Our paper using this workflow: Static Subspace Approximation for Random Phase Approximation Correlation Energies: Applications to Materials for Catalysis and Electrochemistry, https://chemrxiv.org/engage/chemrxiv/article-details/6658bc46418a5379b0b04f64

Let’s begin the tutorials!

- Please log-in to Jupyter Hub for Perlmutter like yesterday

- Please copy a new version of the RPA and GW tutorials
  - Look for the RPA Pt+H adsorption tutorial
  - Look for the solvated GW tutorial
  - Descend into each directory, open the README, and begin!

- These jobs will not be run interactively like yesterday
  - The different scripts you run will be submitting jobs to the queue on our workshop reservation
  - Use the “sq” command in your terminal to see the status of your jobs after running any “XX_run_job.sh” command