What's New in Berkeley GW
Excited State Code

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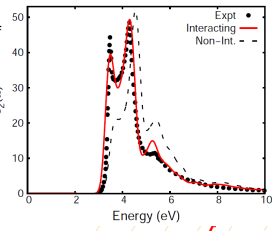
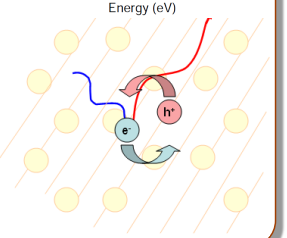
Introduction

Standard DFT approaches fail to capture excited state properties of materials. Such properties are crucial for predicting important material properties related to energy physics such as electron transport, photovoltaic and solid-state lighting potential etc…The GW/Bethe-Salpeter Equation (GW-BSE) method has become one of the standard theoretical approaches for predicting these properties. However, it has been long thought of as too expensive for calculation on systems with more than ~10 atoms.



The BerkeleyGW code contains an implementation of the GW-BSE method capable of computing 100 atoms with the goal of reaching 1000 atom calculations in the near future.

E.g. for many novel systems, the optical properties are modified substantially by bound or unbound **Excitons**, the excitations of the interaction between an excited electron and a positively charged hole.



Theoretical Approach

Density Functional Theory → **GW Correction** → **Bethe-Salpeter Equation**

Ground state properties within DFT using an approximation for the exchange correlation functional and a pseudopotential method.

Quasiparticle properties with the GW approximation to the self-energy operator, Σ=iGW. G is the one electron Green's Function and W is the screened Coulomb interaction.

Two-particle excited state properties through a Beth-Salpeter Equation. Yields excitation spectra!

Computational Problem

$$\left(\frac{-\nabla^2}{2}+V_{ion}+V_{hartree}+V_{x^{LDA}}\right)\psi_{nk}=E_{nk^{LDA}}\psi_{nk}$$

DFT Kohn-Sham eigenvalue equation solved in plane wave basis for lowest eigenvalues and eigenfunctions.

$$\left(\frac{-\nabla^2}{2}+V_{ion}+V_{hartree}+\Sigma(E_{nk})\right)\psi_{nk}=E_{nk}\psi_{nk}$$

GW Dyson equation for corrected eigenvalues and functions. Solved in basis of Kohn-Sham eigenstates.

$$(E_c-E_v)A^{s}_{vc}+\sum_{v'c'}K^{AA}_{vc,v'c'}(\Omega_s)A^{s}_{v'c'}=\Omega_s A^{s}_{vc}$$

Electron-hole Bethe-Salpeter Equation, solved in basis of 2 particle GW states.

Full-frequency Calculation

Dielectric Matrix (Random Phase Approximation)

$$\epsilon^{r/a}_{GG'}(q,E)=\delta_{GG'}-v(q+G)\chi^{r/a}_{GG'}(q,E)$$

Polarizability

$$\chi^{r/a}_{GG'}(q,E)=\sum_{n}^{occ}\sum_{n'}^{emp}\sum_{k}M'^{*}_{nn}(k,q,G)M'_{nn}(k,q,G')$$
$$\times\frac{1}{2}\left[\frac{1}{E_{nk+q}-E_{n'k}-E\mp i\delta}+\frac{1}{E_{nk+q}-E_{n'k}+E\pm i\delta}\right].$$

Cost:
- Each sum is $O(N^4)$
- Resum for each distinct E
- Brute-force is expensive for evaluating

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

Efficient approximation (Shsikin & Kresse 06, T. Miyake & Aryasetiawan 00):
- Goal: Reduce the number of frequency-dependent χ evaluations
- Techniques:
  - Hilbert transform

$$\chi_{GG'}(q,E)=\int_0^\infty dE'\chi^{s}_{GG'}(q,E')\left[\frac{1}{E-E'+i\delta}-\frac{1}{E+E'+i\delta}\right]$$

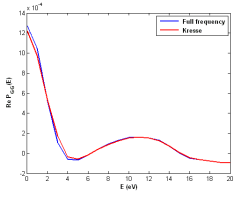
  - Spectral function

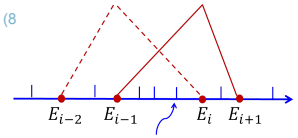
$$\chi^{S}_{GG'}(q,E)=\sum_{n}^{occ}\sum_{n'}^{emp}\sum_{k}M^{*}_{n,n'}(k,q,G)M_{n,n'}(k,q,G')$$
$$\times\tfrac{1}{2}\left[\delta\left(E_{nk+q}-E_{n'k}-E\right)+\delta\left(E_{nk+q}-E_{n'k}+E\right)\right].$$

  - Key observation:
    - $\chi^{S}_{G,G'}(q,E)$ is cheaper to evaluate, i.e., for each E, the sum involves a few n,n' terms
    - A fixed number (k) of $\chi^{S}_{G,G'}(q,E_i), i=1,2,\ldots,k$ is needed for the evaluation of $\chi_{G,G'}(q,E_j)$ for any E_j
    - Each $\Delta_{n,n'}$ contributes to sums covered by two hat functions. So the cost of $\chi^{S}_{G,G'}$ is twice the cost of a static calculation
    - Hilbert transform is much cheaper

$$\chi_{GG'}(q,E_j)=\sum_i t_{ji}\chi^{S}_{GG'}(q,E_i)$$

Example:
Pentacene/Perfluoropentacene Blend (8 molecules, 576 electrons)



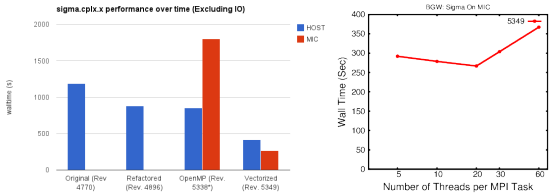


Efficiency

System	#Cores	$\lvert E_j\rvert$	$\lvert E_i\rvert$	Old	New
CO	512	401	301	105	33
PP Blend	10,752	201	56	370k*	22K

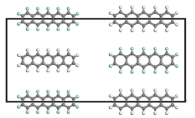
More Parallelism

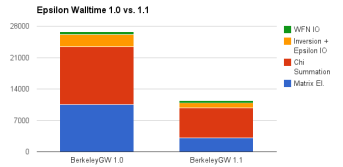
$$\langle n\mathbf{k}|\Sigma^{N}_{\mathrm{CH}}(\mathbf{r},\mathbf{r}';E)|n\mathbf{k}\rangle=\frac{1}{2}\sum_{n''}^{N}\sum_{\mathbf{qGG'}}\langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n''\mathbf{k}-\mathbf{q}\rangle\langle n''\mathbf{k}-\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\mathbf{k}\rangle$$
$$\times\left\{\frac{\Omega^2_{\mathrm{GG'}}(\mathbf{q})}{\tilde{\omega}_{\mathrm{GG'}}(\mathbf{q})\left[E-E_{n''\mathbf{k}-\mathbf{q}}-\tilde{\omega}_{\mathrm{GG'}}(\mathbf{q})\right]}v(\mathbf{q}+\mathbf{G}')\right\}$$



Version 1.1 of BGW introduces new levels of parallelism for DOE's HPC resources – including initial support for GPUs and Xeon-Phi. On-node parallelism via OpenMP, (and initial CUDA support) and improved vectorization support.

The above shows the performance of BerkeleyGW's sigma code on two Xeon Phi cards and 2 Xeons as the code base evolved through various revisions.

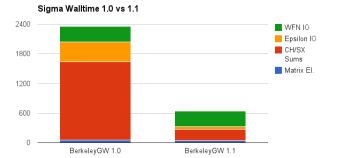




Run on 896 MPI Tasks. Half-Packed Hopper nodes.

BerkeleyGW contains significant performance improvements, including:
- Parallel IO via HDF5
- Improved Memory Locality
- Refactorization to minimize communication.
- Optimized FFT Grids

…Many more small improvements



Run on 1176 MPI Tasks. Packed Hopper nodes.

Red. Empty State Requirement

$$\langle n\mathbf{k}|\Sigma^{\infty}_{\mathrm{CH}}(\mathbf{r},\mathbf{r}';E)|n'\mathbf{k}\rangle=$$
$$\langle n\mathbf{k}|\Sigma^{N}_{\mathrm{CH}}(\mathbf{r},\mathbf{r}';E)|n'\mathbf{k}\rangle+\frac{1}{\gamma}\left(\langle n\mathbf{k}|\Sigma^{Coh/\infty}_{\mathrm{CH}}(\mathbf{r},\mathbf{r}')|n'\mathbf{k}\rangle-\langle n\mathbf{k}|\Sigma^{Coh/N}_{\mathrm{CH}}(\mathbf{r},\mathbf{r}')|n'\mathbf{k}\rangle\right).$$