Excited States and Spectroscopic Properties of Condensed Matter: Theoretical Developments and Computational Challenges

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U.S. DEPARTMENT OF ENERGY | Office of Science

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Scalable Computational Tools for Discovery and Design: Excited State Phenomena in Energy Materials

The objective of our program is to develop and implement new methods and theories to predict electronic excited state phenomena in energy related materials, e.g., materials for photovoltaics, photocatalysis, and electrical energy storage.

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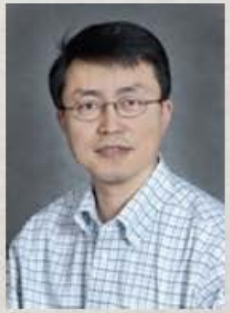

Chao Yang
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Collaborations with FASTMath* and SUPER SciDAC Institutes

Semi-annual Coordination Meetings

U of Texas, Austin, Texas
June 8, 2013

First-Principles Study of Material Properties

Ground-state Properties: (electrons in ground state)

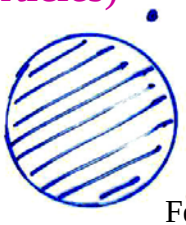
Cohesive
Structural
Vibrational
Magnetic structure
Phase transformations
...

- Density functional theory, QMC, …

Spectroscopic Properties: (behavior of excited particles)

Photoemission
Tunneling
...

- N+1 Particle Problem
- Quasiparticle Approach (GW)



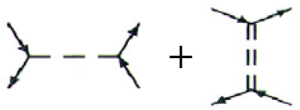
Fermi sea

$\Sigma = iGW$

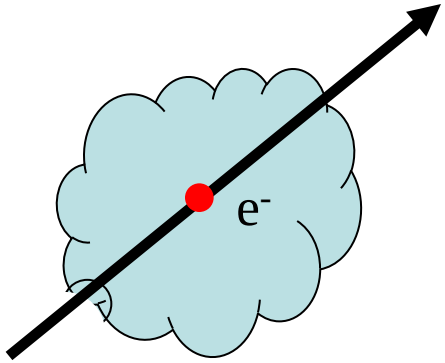
Optical

- N+2 Particle Problem
- Electron-hole interaction (excitonic)

Fermi sea



Ab initio Studies of Quasiparticle Excitations in Transport and ARPES



$$E(\mathbf{k}) = E^0(\mathbf{k}) + \Sigma(\mathbf{k},E)$$

- renormalizes energy dispersion
- gives rise to lifetime

$$A(\mathbf{k},\omega) = \frac{2}{\pi}\frac{-\mathrm{Im}\Sigma(\mathbf{k},\omega)}{\left[\omega - \varepsilon_{\mathbf{k}} - \mathrm{Re}\Sigma(\mathbf{k},\omega)\right]^2 + \left[\mathrm{Im}\Sigma(\mathbf{k},\omega)\right]^2}$$

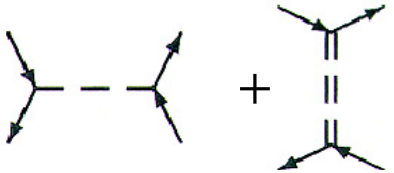
$$\Sigma = \Sigma_{\text{e-e}} \square\square\square \Sigma_{\text{e-ph}} + \ldots$$

First-principles Study of Excited-State Properties: Interacting-particle Green's function approach

Hybertsen and Louie, PRL 1985

- Many-electron interaction effects

  - Quasiparticles and the GW approximation *& beyond*
  - Excitonic effects and the Bethe-Salpeter equation



$$K^{eh} = \frac{\delta V_{\text{Coul}}}{\delta G_1} + \frac{\delta \Sigma}{\delta G_1}$$

v W

- Physical properties computed
  - Quasiparticle dispersion and lifetimes
  - Optical absorption spectra
  - Exciton binding energies and wavefunctions, radiative lifetime, …

Quasiparticle Band Structure Calculations

- Density-functional theory:

$$\left\{-\nabla^2 + V_{\text{ext}} + V_{\text{Coul}} + V_{\text{xc}}\right\}\psi^{\text{DFT}}_{\mathbf{nk}} = \varepsilon^{\text{DFT}}_{\mathbf{nk}}\psi^{\text{DFT}}_{\mathbf{nk}}$$

Hohenberg, Kohn, and Sham 1965

- Green-function approach

$$\left\{-\nabla^2 + V_{\text{ext}} + V_{\text{Coul}} + \Sigma(\varepsilon^{\text{QP}}_{\mathbf{nk}})\right\}\psi^{\text{QP}}_{\mathbf{nk}} = \varepsilon^{\text{QP}}_{\mathbf{nk}}\psi^{\text{QP}}_{\mathbf{nk}}$$

$\Sigma = iG_1W$ GW approximation for the self energy

G_1 one-particle Green function

$W = \epsilon^{-1}v$ screened Coulomb interaction

Hedin 1965, Hybertsen and Louie 1985

- $\Sigma(\mathbf{r}, \mathbf{r'}, \omega)$ - nonlocal, energy-dependent nonHermitian operator
- Large complex eigenvalue problem

GW Approximation

$$\Sigma(\vec{r},\vec{r}';E) = \frac{i}{2\pi}\int W(\vec{r},\vec{r}',\omega)G(\vec{r},\vec{r}',E+\omega)e^{i\delta\omega}d\omega$$

with

$$W(\vec{r},\vec{r}',\omega) = \int v(\vec{r},\vec{r}'')\varepsilon^{-1}(\vec{r}'',\vec{r}',\omega)d^3r''$$

$$G(\vec{r},\vec{r}',\omega) = \sum_{n\vec{k}} \frac{\psi_{n\vec{k}}(\vec{r})\psi^{*}_{n\vec{k}}(\vec{r}')}{\omega - E_{n\vec{k}} - i\delta_{n\vec{k}}}$$

Sum over empty states!

Require:

Full dielectric matrix (local fields)

$$\varepsilon^{-1}(\vec{r}',\vec{r},\omega) \text{ or } \varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega)$$

$$\chi^{0}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{\Omega}\sum_{n,n',k} f_{n,k}(1-f_{n',k+q})\times\left[\frac{\langle n,\mathbf{k}|\, e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\,|n',\mathbf{k}+\mathbf{G}\rangle\,\langle n',\mathbf{k}+\mathbf{G}'|\, e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}\,|n,\mathbf{k}\rangle}{\varepsilon_{n,\mathbf{k}}-\varepsilon_{n',\mathbf{k}+\mathbf{q}}+\hbar\omega+i\hbar\alpha}+\text{c.c.}\right].$$

Hybertsen and Louie (1985)

Calculation of Optical Absorption Spectrum

- Coupled electron-hole excitations:

$$|S\rangle = \sum_{v}^{\text{elec}} \sum_{c}^{\text{hole}} A^S_{vc}\, \hat{a}^\dagger_v\, \hat{b}^\dagger_c\, |0\rangle$$

$|0\rangle$ ground state of many-electron system

$\hat{a}^\dagger_v$, $\hat{b}^\dagger_c$ creates quasi-hole, -electron

A^S_{vc} coupling coefficients

v = n**k** (occupied)

c = n'**k** (unoccupied)

- The Bethe-Salpeter Equation for the two-particle Green's function G_2 yields:

$$(\varepsilon^{\text{QP}}_c - \varepsilon^{\text{QP}}_v) A^S_{vc} + \sum_{v'c'} \langle vc|K^{eh}|v'c'\rangle A^S_{v'c'} = \Omega^S A^S_{vc}$$

M. Rohfling and S. G. Louie, PRL (1998)

$\varepsilon^{\text{QP}}_c$, $\varepsilon^{\text{QP}}_v$ single-quasiparticle energies

K^{eh} electron-hole interaction

$\Longrightarrow$ Ω^S excitation energies

- Electron-hole interaction kernel:

$$K^{eh} = \frac{\delta V_{\text{Coul}}}{\delta G_1} + \frac{\delta \Sigma}{\delta G_1}$$

$\frac{\delta V_{\text{Coul}}}{\delta G_1} \rightarrow v$, $\frac{\delta \Sigma}{\delta G_1} \rightarrow W$

- $\Longrightarrow$ Optical absorption spectrum: $\epsilon_2(\omega)$

- K - large, nonHermitian matrix with very fine **k** sampling
- K can have dimensions as large as ~10^5

Program Activities

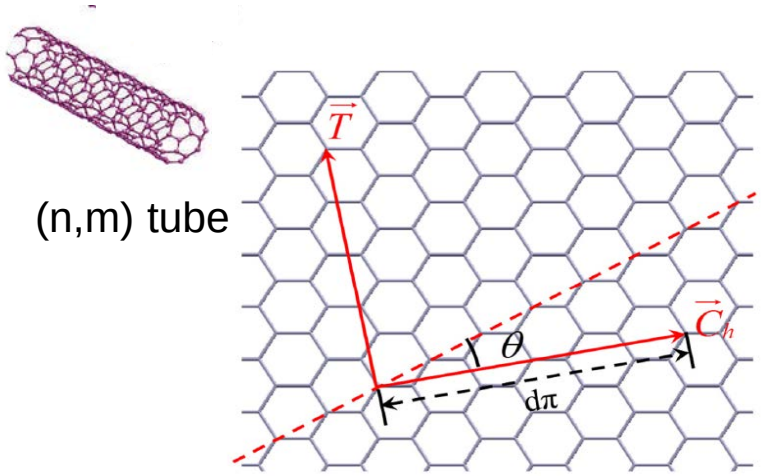
- New theories and methods for properties previously inaccessible by *ab initio* excited-state calculations for solids

- Algorithmic and code developments to address computational challenges for the new properties and in complex, large systems

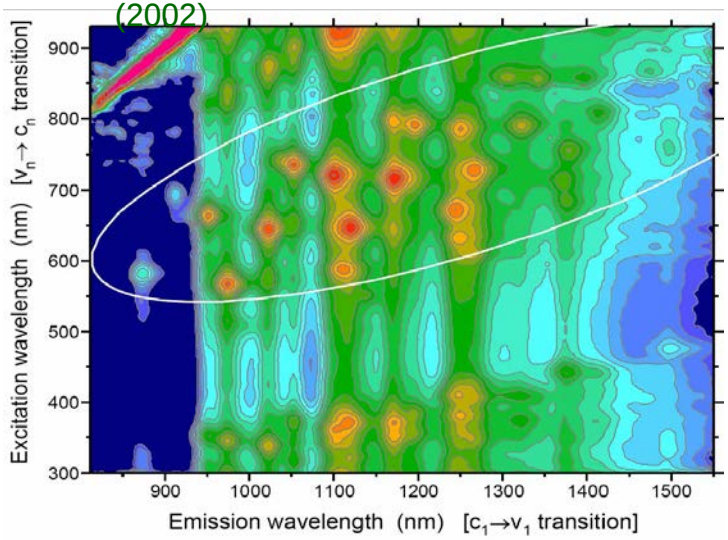
- Applications to materials systems of DOE/BES interests

Photo-response of Nanostructures

- Interesting fundamental physics --many-body, dimensionality, and structural effects
- Useful in characterizing the nanostructures
- Possible applications -- e.g., optoelectronics, sensors, imaging, photovoltaics, energy conversion/generation, etc.

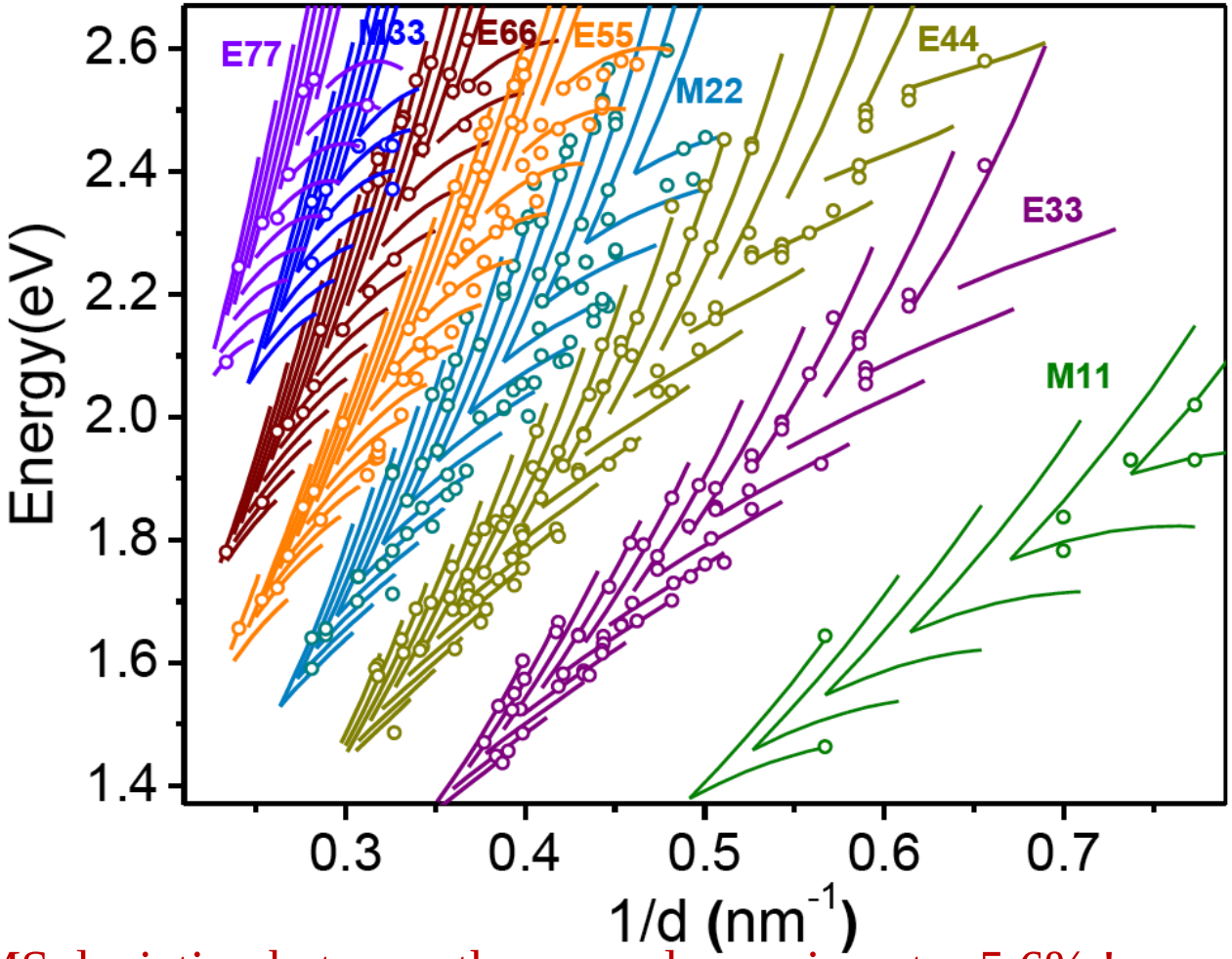


Photoluminescence: Rice group (2002)



Optical Properties of Single-Walled Carbon Nanotubes: GW-BSE Theory vs. Experiment

E33 to E77 Rayleigh scattering data from Feng Wang's group (Nature Nanotech. 2012) + E11 and E22 photoluminescence data from Bachilo *et al. Science* **298**, 2361 (2002): **total of 308 transitions!**



For any (n,m) SWCNT:

- QP excitation energies
- exciton binding energies
- optical transition energies
- excited exciton states
- optical oscillator strengths, …

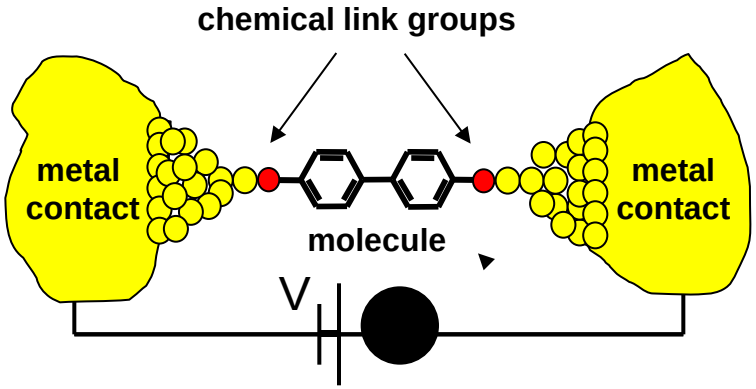
RMS deviation between theory and experiment = 5.6% !

No empirical parameters!

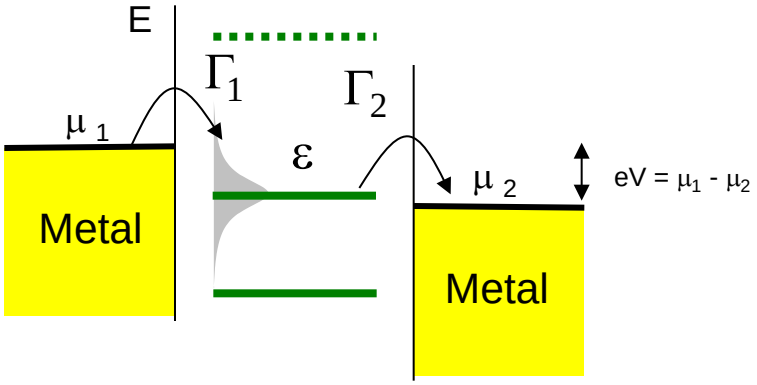
Deslippe, Capaz and Louie (2013)

Single-molecule conductance

Metal-molecule junction



Microscopic picture



- Contact chemistry, electronic structure control transmission
- The energy (ε) and width of its levels (Γ) controls junction transmission & resistance

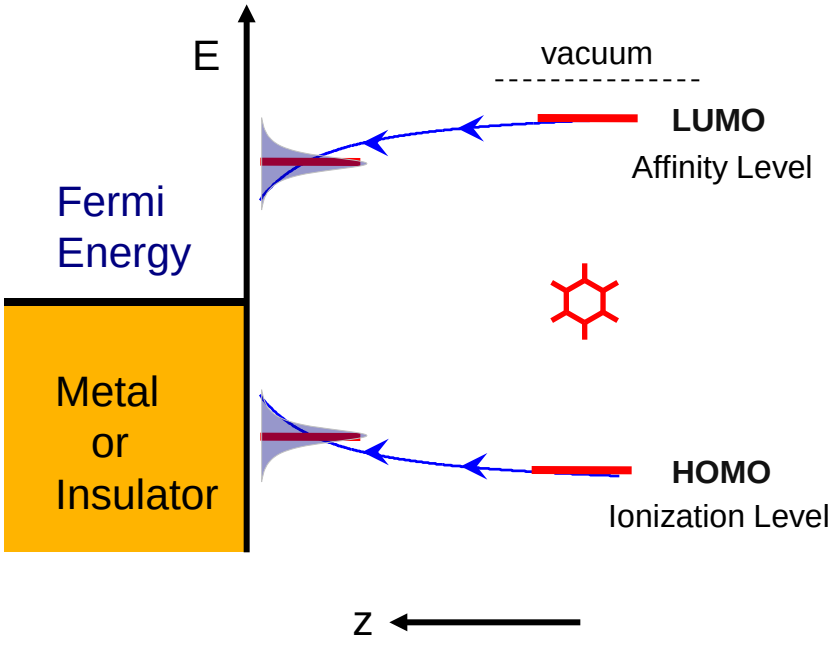
Major issue: DFT-based methods yield conductance which is often orders of magnitude too large, in particular in the tunneling regime

Cause = neglect of self energy effects

Neaton, Hybertsen, Louie, PRL (2006)
Quek, Choi, Louie, Neaton, Nano Lett (2009)

Level alignment at material-molecule contacts

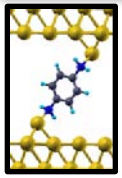
Energy level diagram

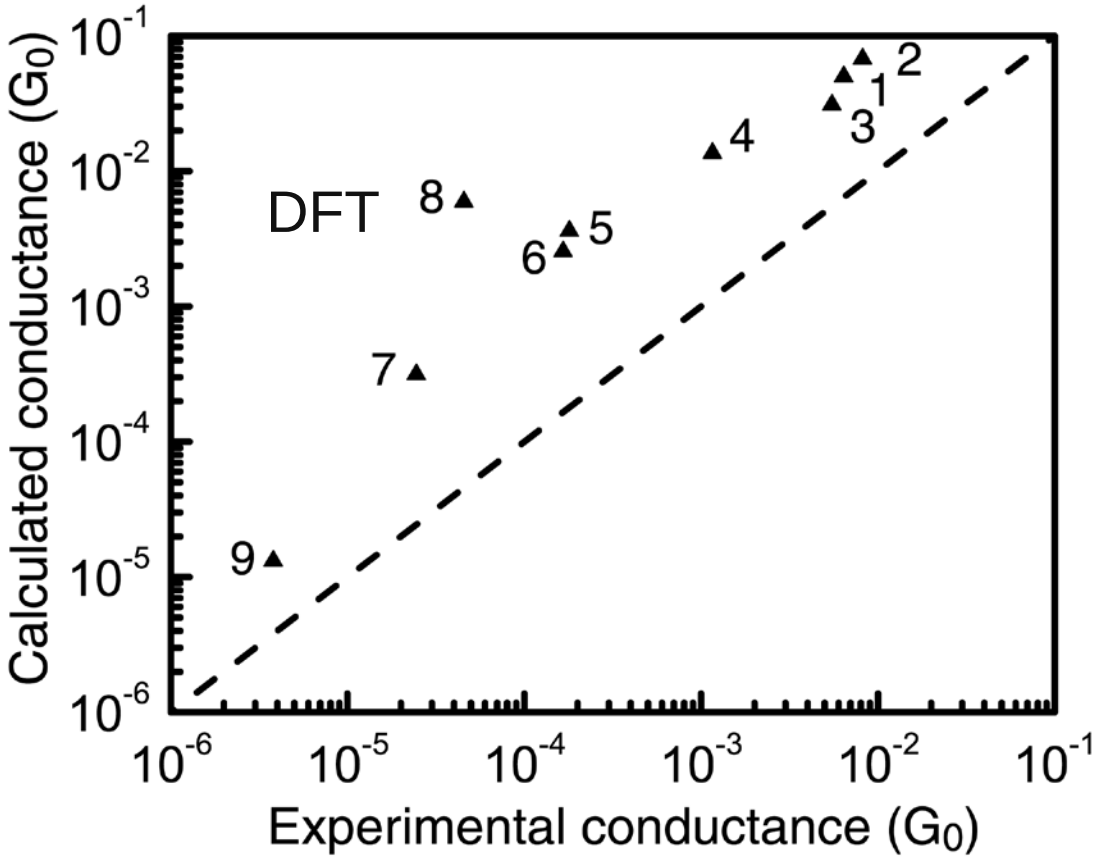


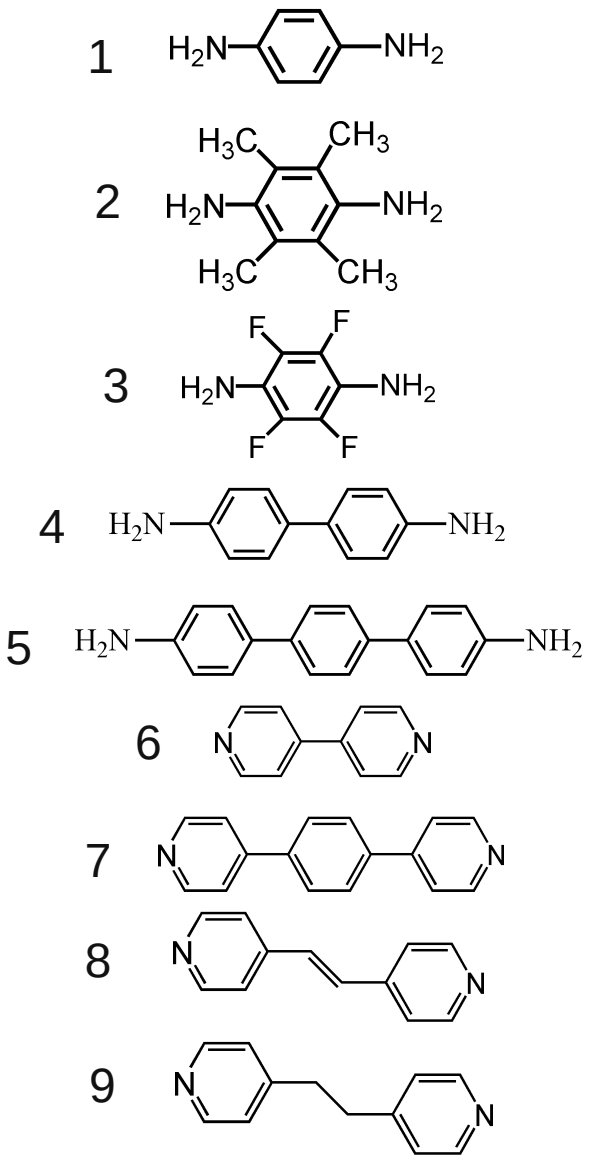
Physical effects

- Interfacial charge transfer (dipoles)
- Quantum mechanical (electronic) coupling
- Electron correlation (**self energy**) effects

Calculated Conductance for Different Molecules

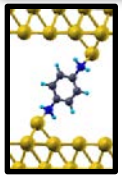




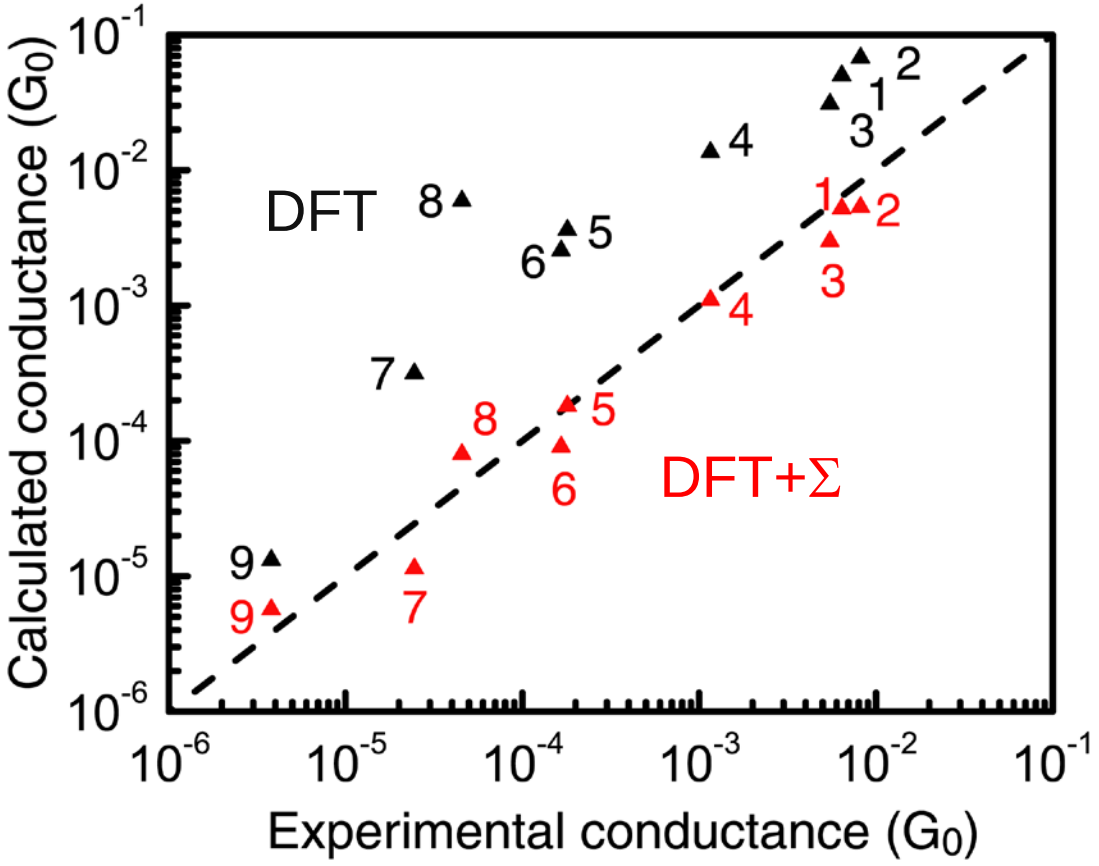


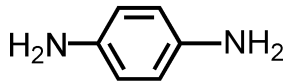
Quek, Strubbe, Choi, Louie, Neation (2013)
Expt: Venkataraman group

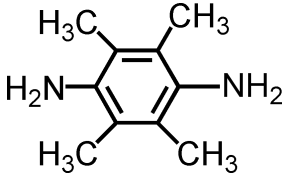
Calculated Conductance for Different Molecules

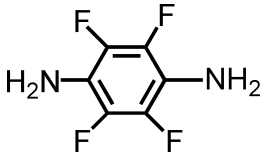


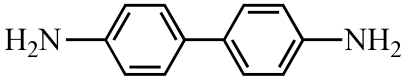
$$H \rightarrow H + \sum_{mol} \Sigma_{mol} \left|\psi_{mol}\right\rangle\left\langle\psi_{mol}\right|$$



1 

2 

3 

4 

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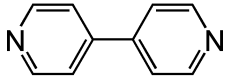
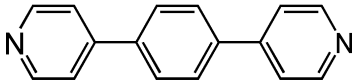
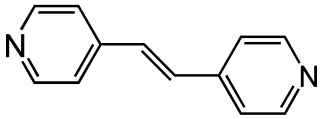
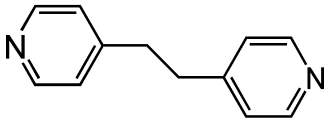
6 

7 

8 



Similar improvement in *molecular length dependence of G* and in *thermopower* is found!

Program Activities

- New theories and methods for properties previously inaccessible by ab initio excited-state calculations for solids
  - *Spinor wavefunction formulation and codes for solids with strong spin-orbit coupling*
  - *Quasiparticle excitations in degenerate ground-state (open shell) systems (e.g., magnetic defects)*
  - *GW+cumulant (GW+C) approach for satellite structures* ✓
  - *Spin fluctuations in electron self energy of magnetic systems*

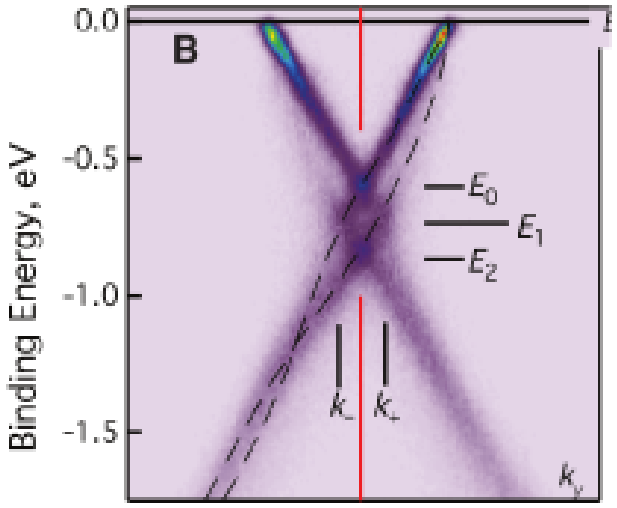
  …

- Algorithmic and code developments to address computational challenges for the new properties and in complex, large systems

- Applications to materials systems of DOE/BES interests

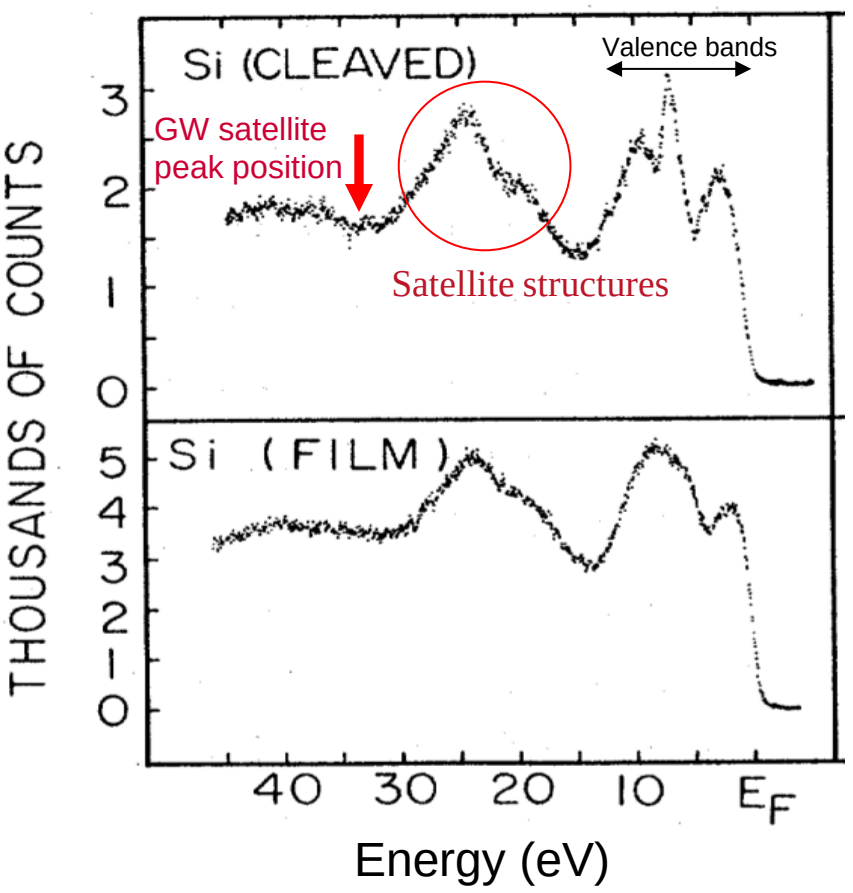
Satellite structure in Si and dope graphene

ARPES



Bostwick et al., Science 328 (5981): 999-1002 (2010)

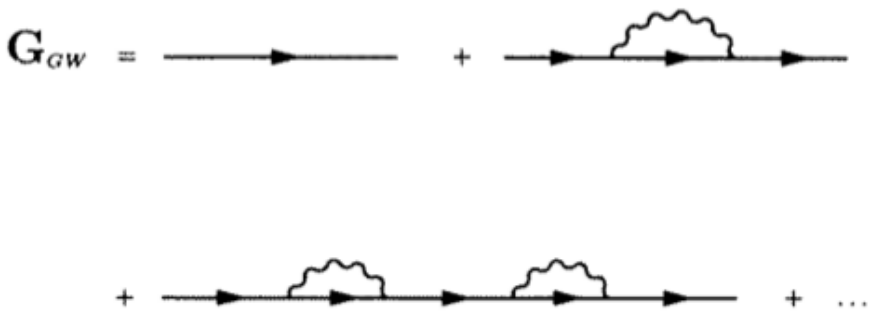
Graphene satellite structure



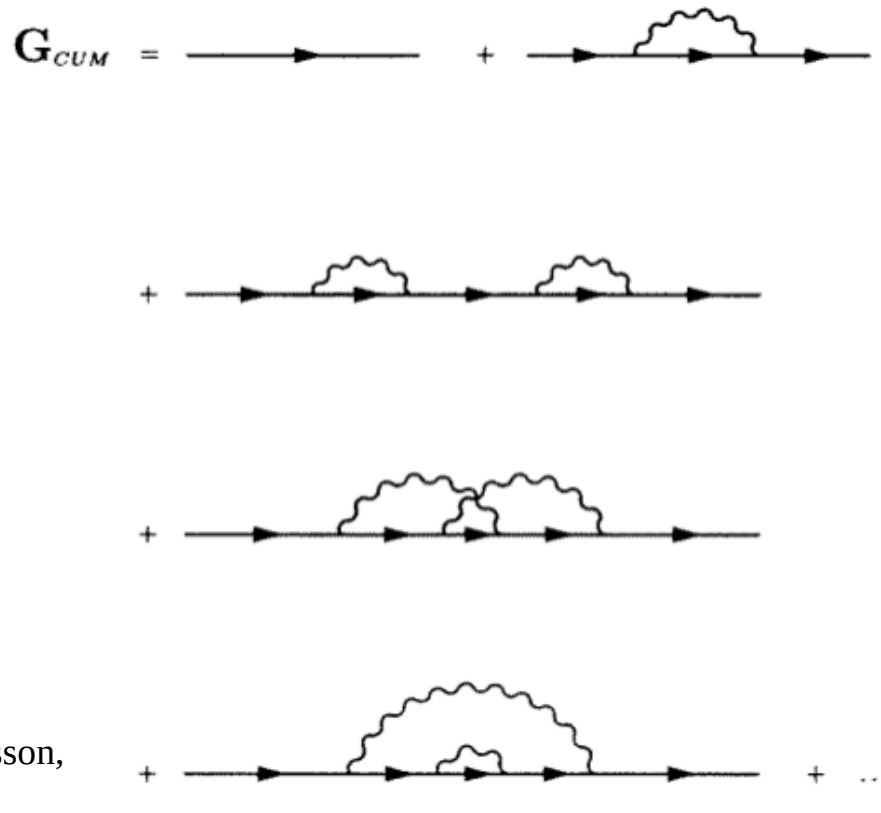
L. Ley, et al PRL 29, p.1088–1092 (1972)

Feyman diagrams in GW and GW+C

$$G = G^0 + G^0 \Sigma G$$



GW approx.



GW + cumulant expansion approx.

Figure after Aryasetiawan & Gunnarsson, Rep. Prog. Phys (1998)

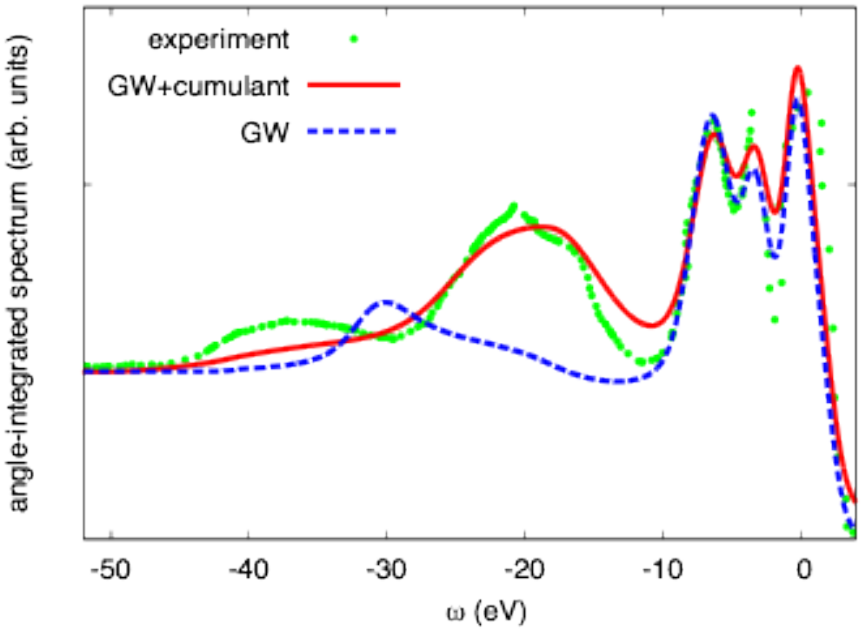
GW+cumulant theory for plasmon satellites

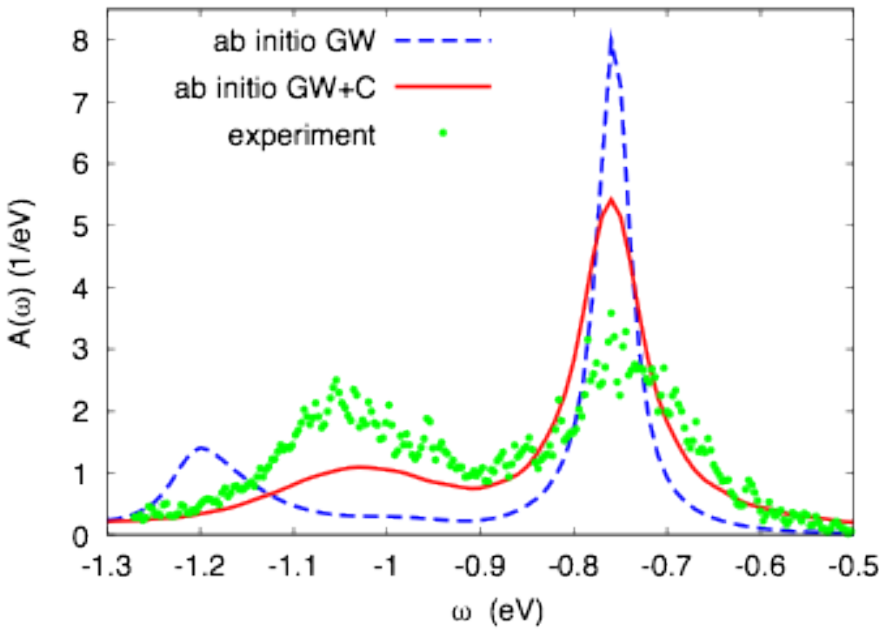
GW+cumulant Green's function:

$$G_{nk}(t) = i\Theta(-t)e^{-i\epsilon_{nk}t+C_{nk}(t)}$$

$$C_{nk}(t) = -it\Sigma_{nk}(t)(E_{nk}) + \frac{\partial\Sigma_{nk}(E_{nk})}{\partial\omega} + \int_{-\infty}^{\mu}\frac{d\omega}{\pi}\frac{\mathrm{Im}\Sigma_{nk}(\omega)}{(E_{nk}-\omega-i\eta)^2}e^{i(E_{nk}-\omega)t}$$

Application: silicon and doped graphene





Lischner, Vigil, and Louie (2012)

Program Activities

- New theories and methods for properties previously inaccessible to ab initio excited-state calculations for solids
- Algorithmic and code developments to address computational challenges for the new properties and in complex, large systems
  - *PARSEC-BerkeleyGW interface*
  - *New/improved k-point interpolation of el-hole kernel for GW-BSE*
  - *Non-Hermitian GW-BSE methodology: Going beyond Tamm-Dancoff Approximation* ✓
  - *Reduction/elimination of the empty states requirement*
  - *Accurate and efficient full frequency calculation for ε and Σ*
  - *Diagonalization of large, non-sparse matrices* ✓
  - *Efficient codes for current and future high performance machines* ✓

  …
- Applications to materials systems of DOE/BES interests

Non-Hermitian Bethe-Salpeter Equation

- The Bethe-Salpeter equation (BSE) Hamiltonian has the following structure:

$$H_{BSE} = \begin{bmatrix} R & C \\ -C^* & -R^* \end{bmatrix}$$, C is Hermitian, and R can be non-Hermitian.

- BerkeleyGW originally supported the BSE within the Tamm-Dancoff approximation (TDA), i.e., C=0 and R Hermitian.

- Recent progress and improvements:
  - We can now solve the full BSE without the Tamm-Dancoff approximation.
  - Current implementation is serial, still need efficient way to solve in parallel.

Matrix diagonalization techniques

- Excited state calculations typically need many eigenpairs (both occupied and empty states)
- Bottleneck in existing solver: Rayleigh-Ritz procedure, i.e. compute eigenpairs of a projected problem (dimension can be as large as 100,000)
- Two new strategies:
  - Spectrum slicing: divide spectrum into many pieces and compute eigenvalues within each in parallel (see poster)
  - Use penalized trace minimization (see poster)

BerkeleyGW 1.1

Goals:

Optimize the traditional GW/BSE approach for today's DOE powered HPC resources.

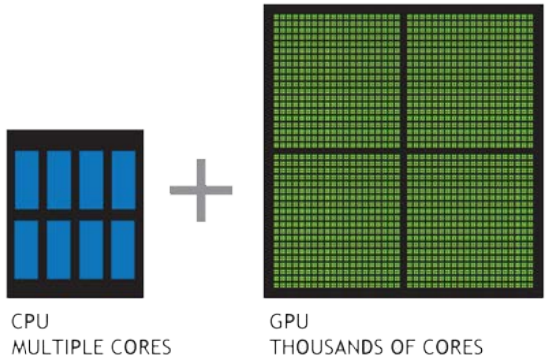
Prepare the code for DOE's next generation machines.

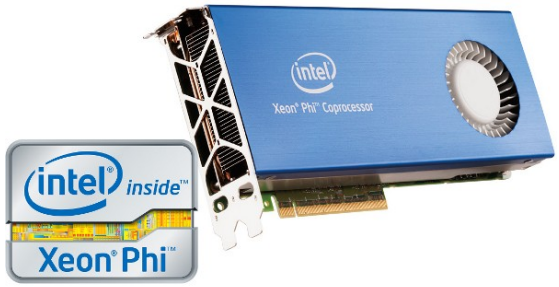
Science Codes Face Common Challenge of Changing Architecture

For the last decade, we had massively parallel machines with MPI as standard programming method for parallelism.

We are now in an age of multi-core nodes and many-core accelerators.

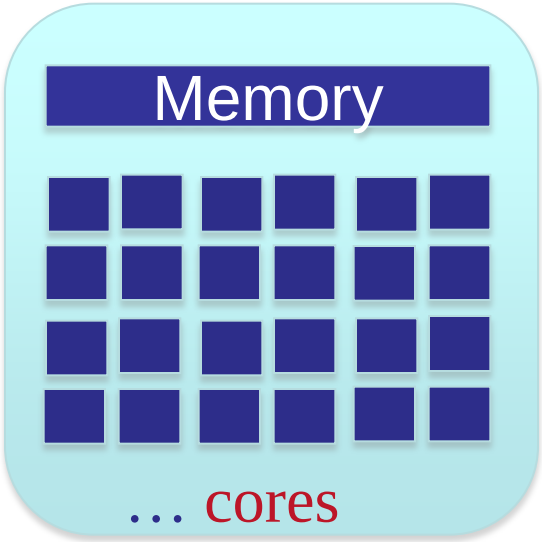
To study large physical systems of interest, and get the most out of HPC resources, we need to exploit on node parallelism effectively: multi-core and vector parallel.





How BerkeleyGW Uses MPI + OpenMP

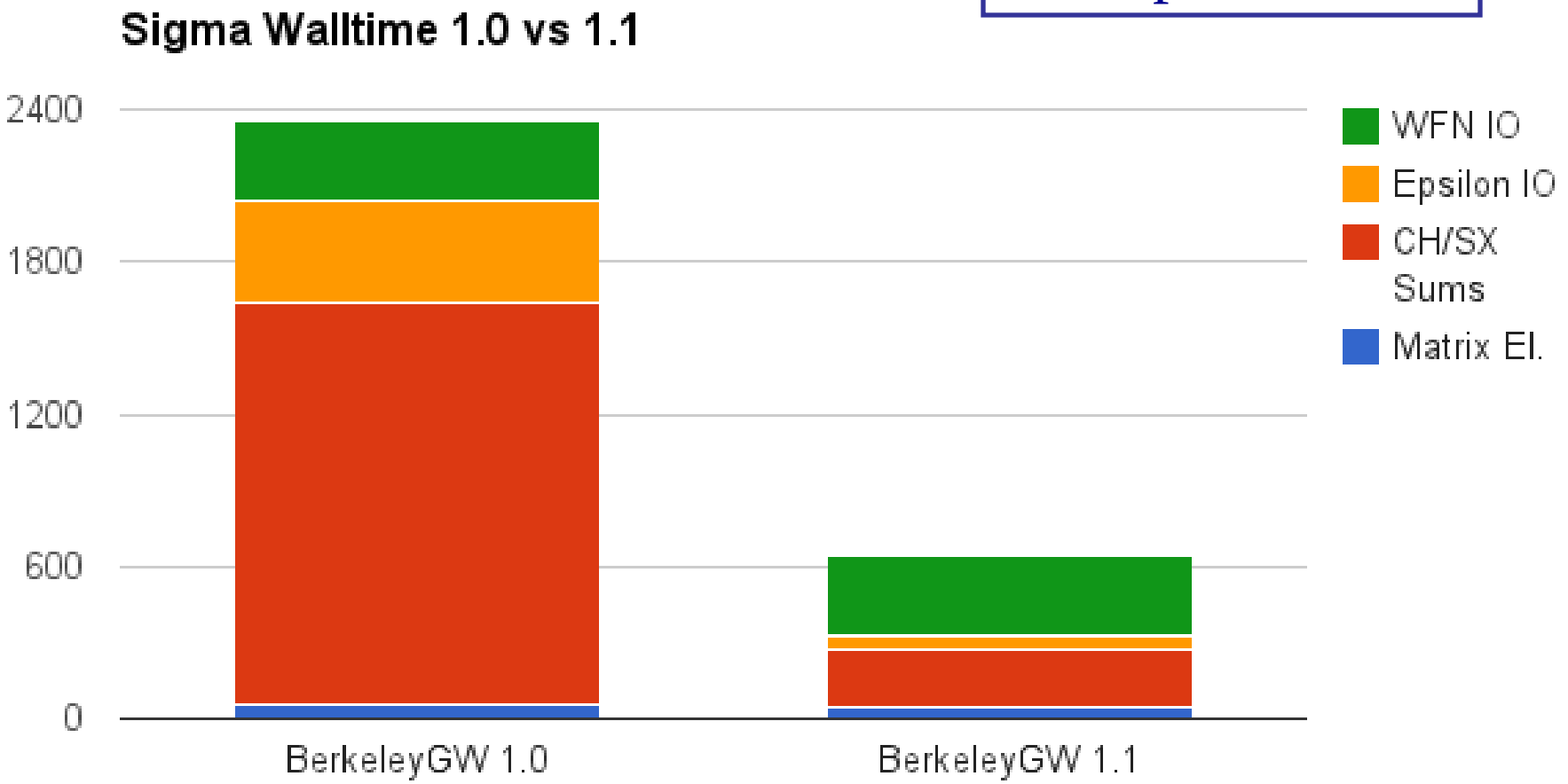
- Eliminates memory overhead of previously assigning every MPI tasks to each core. Critical for studying large systems.
- Use MPI only at the node level. Fewer MPI tasks also reduce communication time
- Takes advantage of on-node parallelism. Supports > 100 threads.
- Using custom, hybrid MPI-OpenMP routines for FFTs, Matrix-Multiplication, Inversion and Diagonalization.



GPUs and Intel Xeon-Phi support > 100 of hardware threads.

BerkeleyGW 1.0 vs. 1.1 – NERSC Hopper

4x improvement!



(See poster for details.)

BerkeleyGW 1.1 has initial support for both GPU and Xeon-Phi

Program Activities

- New theories and methods for properties previously inaccessible to ab initio excited-state calculations
- Algorithmic and code developments to address computational challenges in complex, large systems
- Applications to materials systems of DOE/BES interests
  - *Chromophore or dye molecules in gas-phase, in solution, or at an oxide surface*
  - *Solvents, e.g. water or electrolyte, in contact with an oxide or metal electrode*
  - *Molecular junctions and self-assembled monolayers*
  - *Multicomponent inorganic semiconductor nanostructures*
  - *Transition metal oxides, with defects and dopants*
  - *Nanophase crystals and clusters appropriate for photovoltaic applications*
  - *Organic molecular crystals and assemblies, and donor-acceptor molecular interfaces*

BerkeleyGW package:

- Suite of codes based on GW and GW+BSE methods
- Quasiparticle and optical properties (up to hundreds atoms)
- Interfaces with PARATEC, Quantum Espresso,

  PARSEC, SIESTA, etc.
- Available to community free -- *www.berkeleygw.org*
- Hands-on workshop on BerkeleyGW – Nov 22-23, 2013, at NERSC in Berkeley