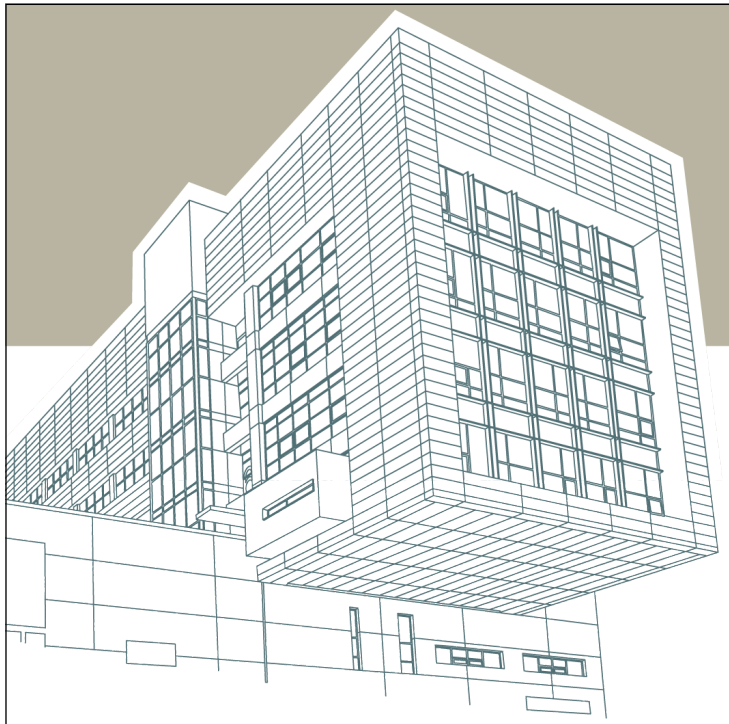


Lawrence Berkeley National Laboratory

The Molecular Foundry

Theory & Simulation of Light-Matter Interactions (& Charge Transport) at Nanoscale Interfaces

Jeff Neaton
Molecular Foundry, LBNL

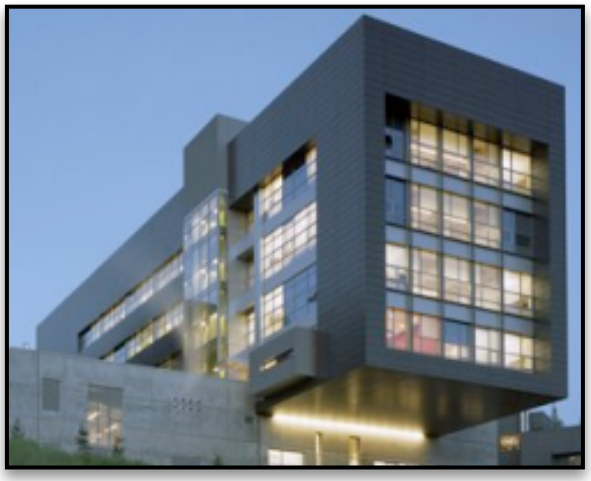
2010 BES NERSC Requirements Workshop

Acknowledgements

Collaborators

Steven Louie, UCB/Foundry
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Hyuk Choo, LBNL
Martina Dell'angela,TASC
Ying Hu, Rice
Masha Kamenetska, Columbia
Alberto Morgante, TASC
Jim Schuck, Foundry





Molecular Foundry, LBNL

Molecular FOUNDRY
A NANOSTRUCTURES USER LABORATORY

Some "Grand" Computational Challenges

Light-Matter Interactions in Real Materials

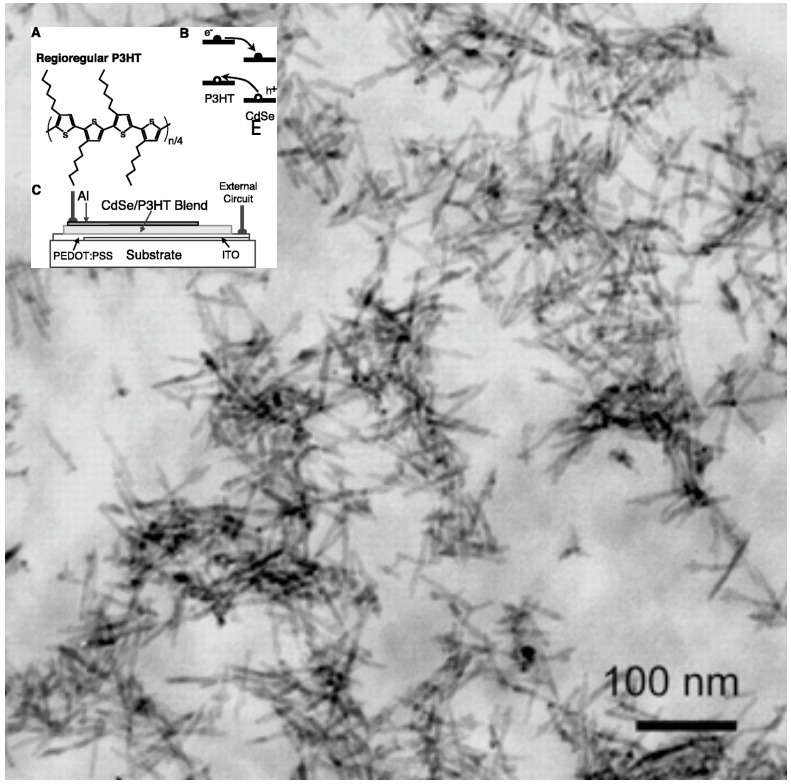
- Large systems: Nanoscale interfaces relevant to solar
- Electron-hole interactions
- Connection to ultrafast spectroscopies

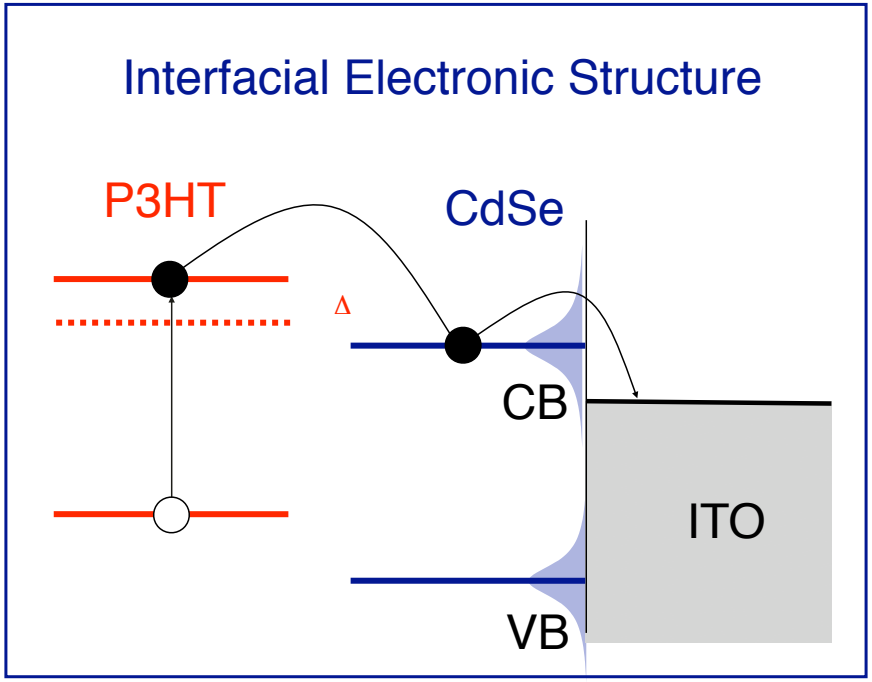
Charge Transport in Real Materials

- Beyond-DFT input
- Nonequilibrium and finite bias

Towards Structure-Function Relationships for Heterogeneous Nanoscale Assemblies

Hybrid Organic-Inorganic Nanoscale Solar Cell



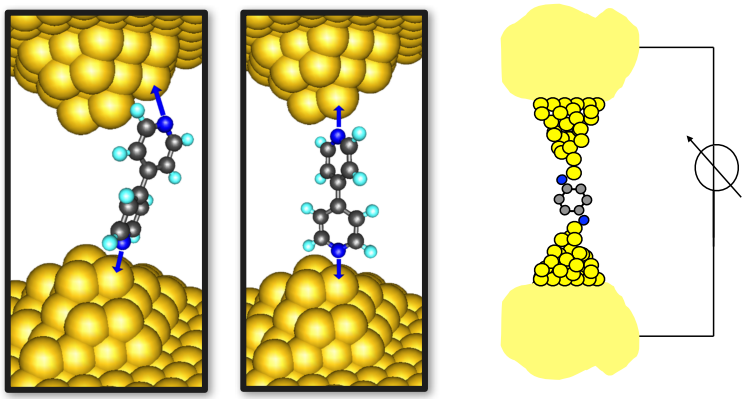


Alivisatos group, Science **295**, 2425 (2002)

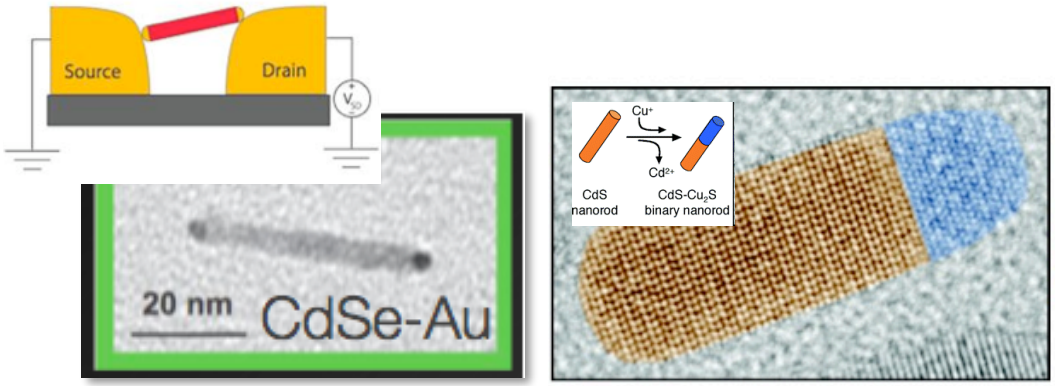
- Function → Interfacial atomic/electronic structure, chemistry
- High density of nanoscale interfaces

Single-Nanostructure Characterization

Charge Transport



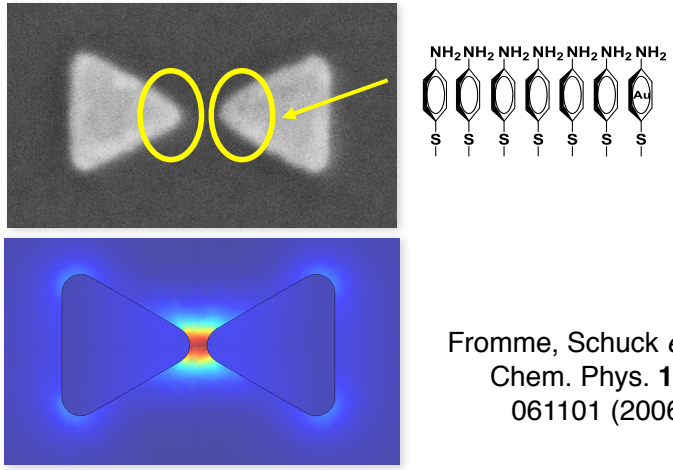
Quek *et al.* Nature Nano. **4**, 230 (2009)



Sheldon et al, *Nano Lett* **9**, 3676 (2009); Sadtler et al, *JACS* **131**, 5285 (2009)

Optical/Vibrational Spectroscopy

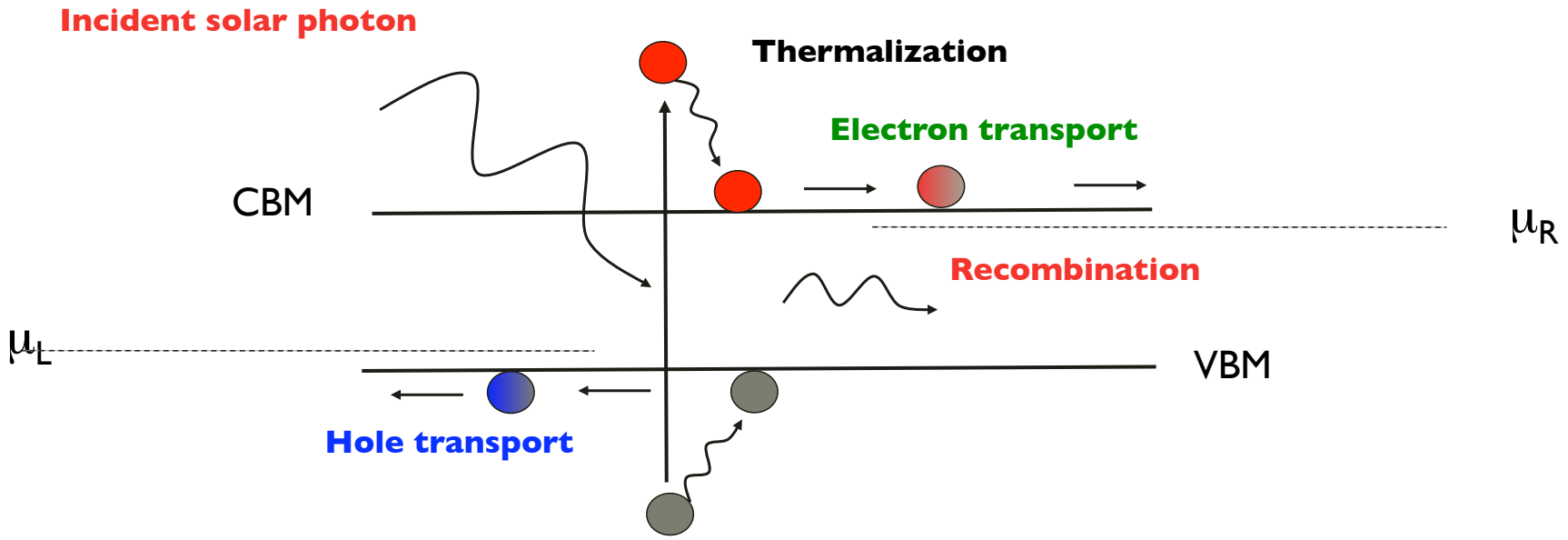
Plasmonics, Raman



Fromme, Schuck *et al,* J. Chem. Phys. **124**, 061101 (2006)

- Structure ↔ Function
- Need insight into interfacial electronic structure to understand measurements

Excitations at Interfaces in Solar Energy Conversion



- Solar-to-electric conversion involves <u>both</u> **neutral** and **charged** excitations (absorption, charge separation, charge transport, charge injection)
- DFT can fail to describe both types of excitations
- Dissipation, kinetics: Electron-phonon interactions are also central

"First-Principles" Beyond-DFT Studies of Nanomaterials

- **"Ground-state" energetics**

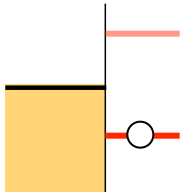
  - Structure
  - Vibrational properties, phonons
  - Polarization, magnetization
  - Underestimates band gaps

Density Functional Theory
(LDA, GGA, B3LYP, etc)

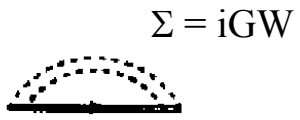
Codes VASP, SIESTA, Pwscf, Paratec, etc

- **Spectroscopic properties** (excited states & transport)

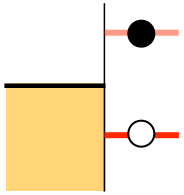
  - Photoemission
  - Transport



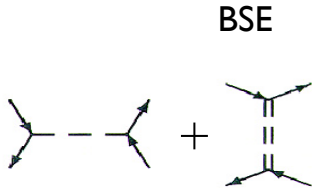
• N+1,N-1 particles
• Quasiparticle approach



  - Optical absorp.



• N+2 particles
• Electron-hole interaction (excitons)



See Also TDDFT, QMC, DMFT

GW approach

- Quasiparticle Hamiltonian in the GW approximation
  (Hedin, 1965; Hybertsen & Louie, 1985)

$$\left(\mathbf{H}_{KS} - \mathbf{V}_{LDA} + \quad \boldsymbol{\Sigma}\right)\psi_{n\mathbf{k}} = E_{n\mathbf{k}}\psi_{n\mathbf{k}}$$

$$\begin{cases} \boldsymbol{\Sigma} = i\mathbf{G}\mathbf{W} \\ W = \varepsilon^{-1}_{RPA}(\mathbf{q},\omega)V \end{cases}$$



- Perturbative correction to DFT Kohn-Sham orbitals & energies
- GW self-energy content (electron addition/removal)

$$\boldsymbol{\Sigma}(\mathbf{r},\mathbf{r}';E) = \boldsymbol{\Sigma}_X + \boldsymbol{\Sigma}_{SX} + \boldsymbol{\Sigma}_{CH}$$

Fock exchange

Dynamically-screened exchange

Dynamical polarization response

➪ Physically-motivated, balanced treatment of correlation in different environments

➪ No adjustable parameters, reasonable scaling (~N_G^4)



Hybertsen & Louie (1985)
BerkeleyGW code

Bethe-Salpeter Equation (BSE) Approach

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}})A^S_{vc\mathbf{k}} + \sum_{v'c'\mathbf{k}'} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle A^S_{v'c'\mathbf{k}'} = \Omega^S A^S_{vc\mathbf{k}}$$

K^{eh} includes exchange and attractive screened direct interactions

Form of e.g. two-particle states

$$|S\rangle = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} |vc\mathbf{k}\rangle$$

Dielectric function (absorption):

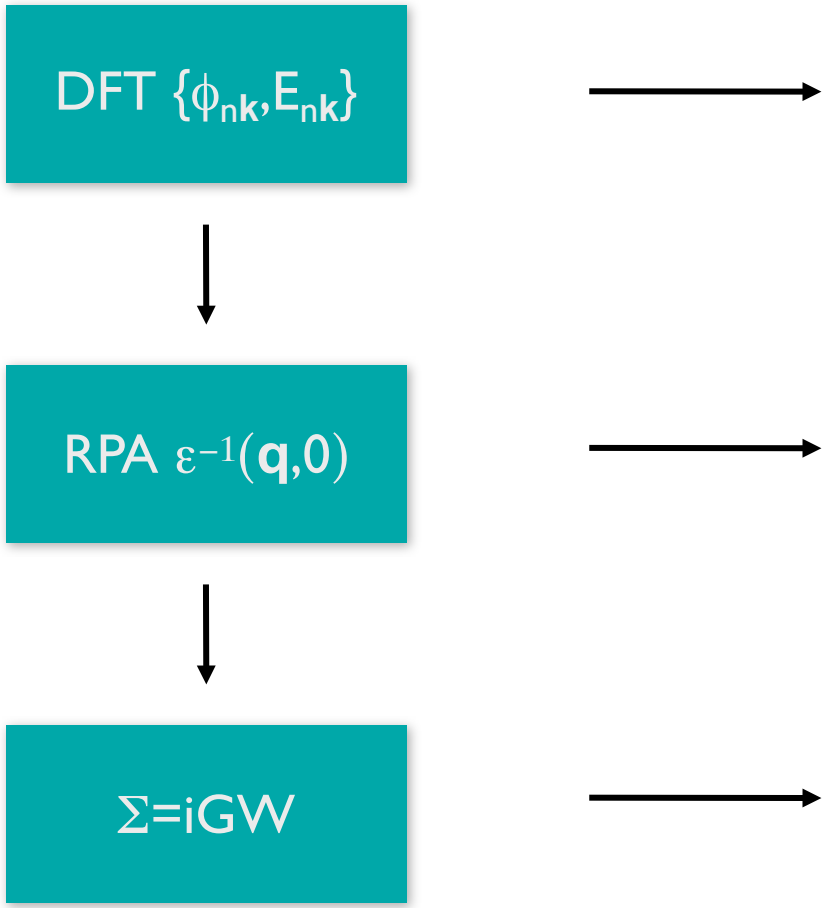
$$\varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_S \left|\vec{\lambda} \cdot \langle 0|\vec{v}|S\rangle\right|^2 \delta(\omega - \Omega_S)$$

Polarization vector $\vec{\lambda} = A/\vec{A}$

$\vec{v} = i/\hbar[H, \vec{r}]$ Single-particle velocity operator

Rohlfing & Louie (2000)
BerkeleyGW code

BerkeleyGW Implementation & Scaling

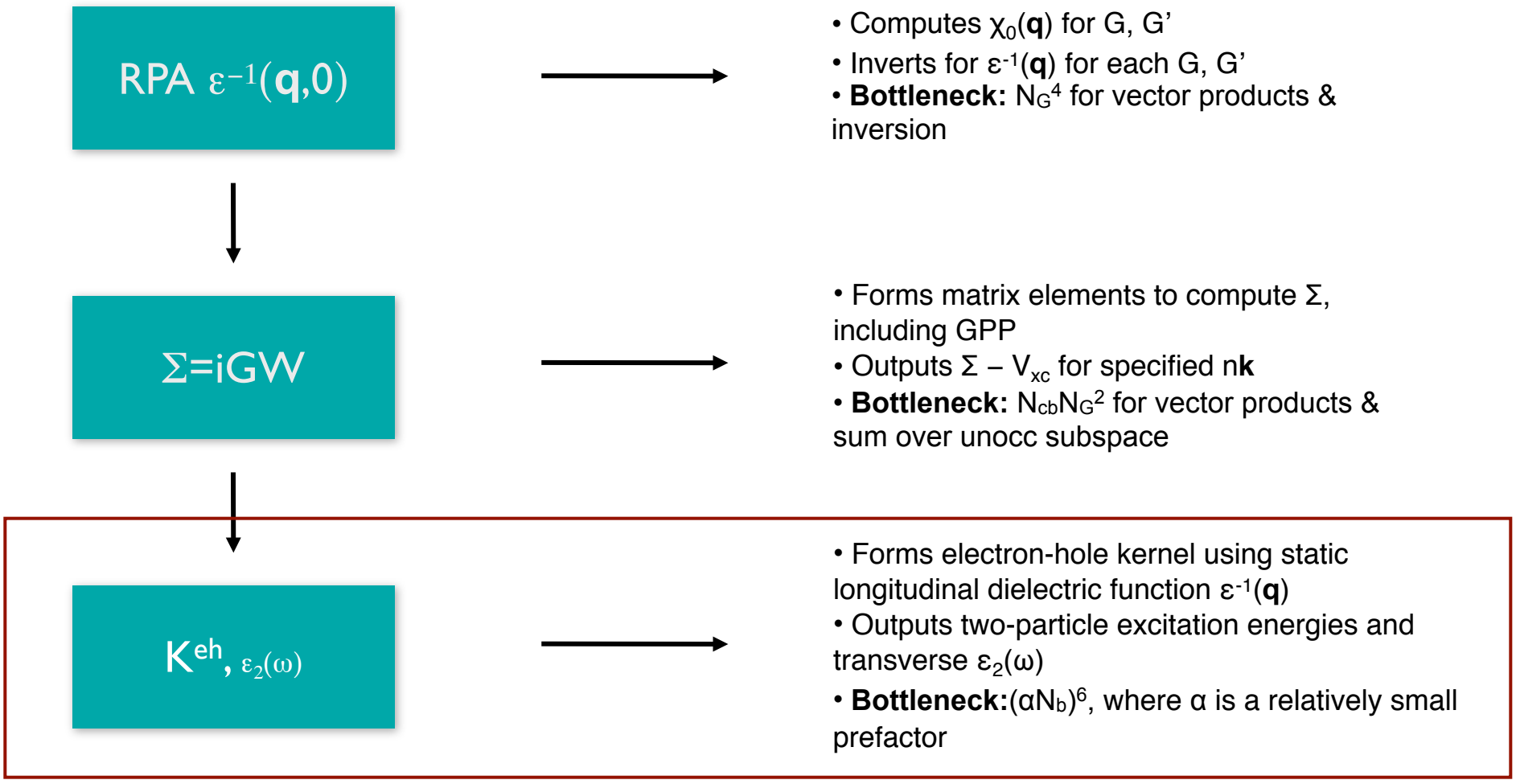


- SCF for ground-state (PW, NC-PPs)
- NSCF for 100-1000's of empty states
- **Bottleneck:** Iterative diagonalization for unoccupied subspace N_b^3

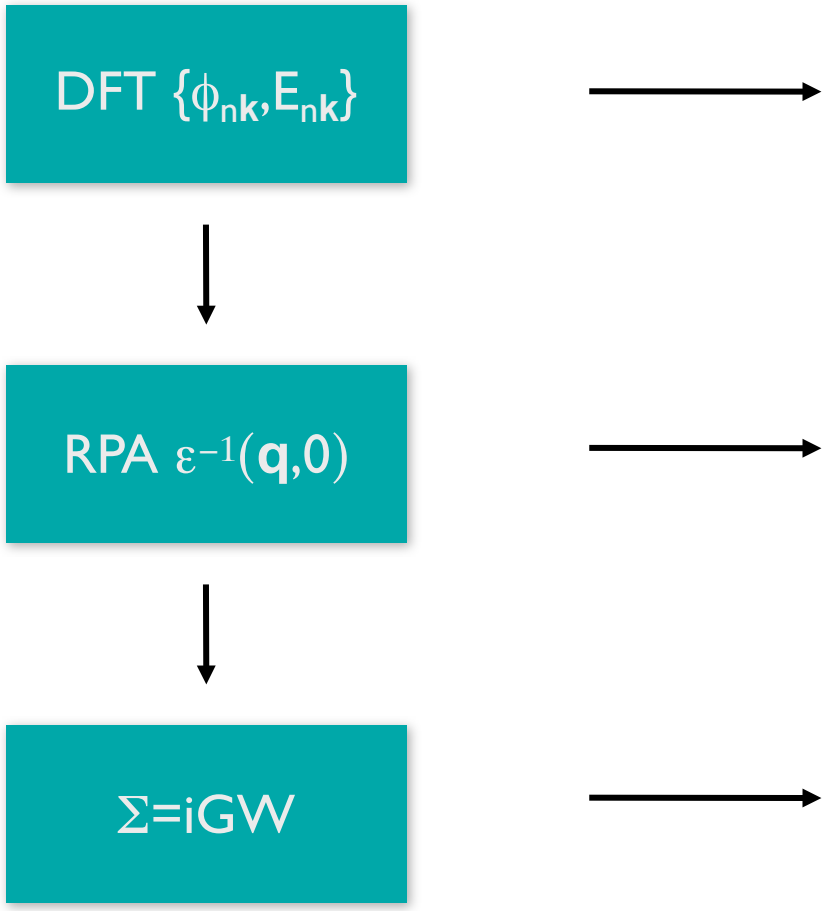
- Compute $\chi_0(\mathbf{q})$ for G, G'
- Inverts for $\varepsilon^{-1}(\mathbf{q})$ for each G, G'
- Plasmon-pole or fully frequency-dependent
- **Bottleneck:** $N_b N_G^3$ for construction of $\chi_0(\mathbf{q})$, plus inversion N_G^3

- Forms matrix elements to compute Σ, including plasmon pole model
- Outputs $\Sigma - V_{xc}$ for specified n**k**
- **Bottleneck:** $N_b N_G^3$ for vector products & sum over unocc subspace

GW/BSE Implementation



GW Implementation & Scaling



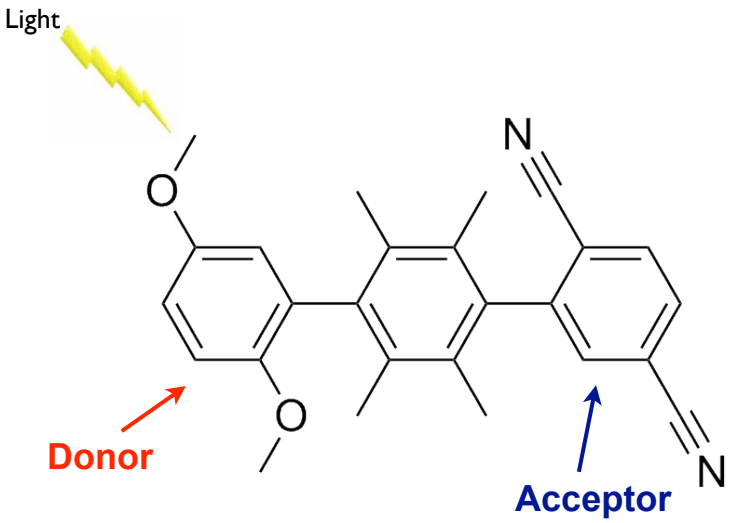
- **Bottleneck:** Iterative diagonalization for unoccupied subspace N_b^3
- 1500 cores, 6hrs for typical run, 150GB total mem, 50GB disk I/O, 20GB online file storage req

- **Bottleneck:** $N_b N_G^3$ for construction of $\chi_0(\mathbf{q})$, plus inversion N_G^3
- 2000 cores, 30 min for typical run,1.5TB total mem, 20GB disk I/O, 50GB online file storage req

- **Bottleneck:** $N_b N_G^3$ for vector products & sum over unocc subspace 2000 cores, 30 min for typical run,500GB total mem, 15GB disk I/O, 50GB online file storage req

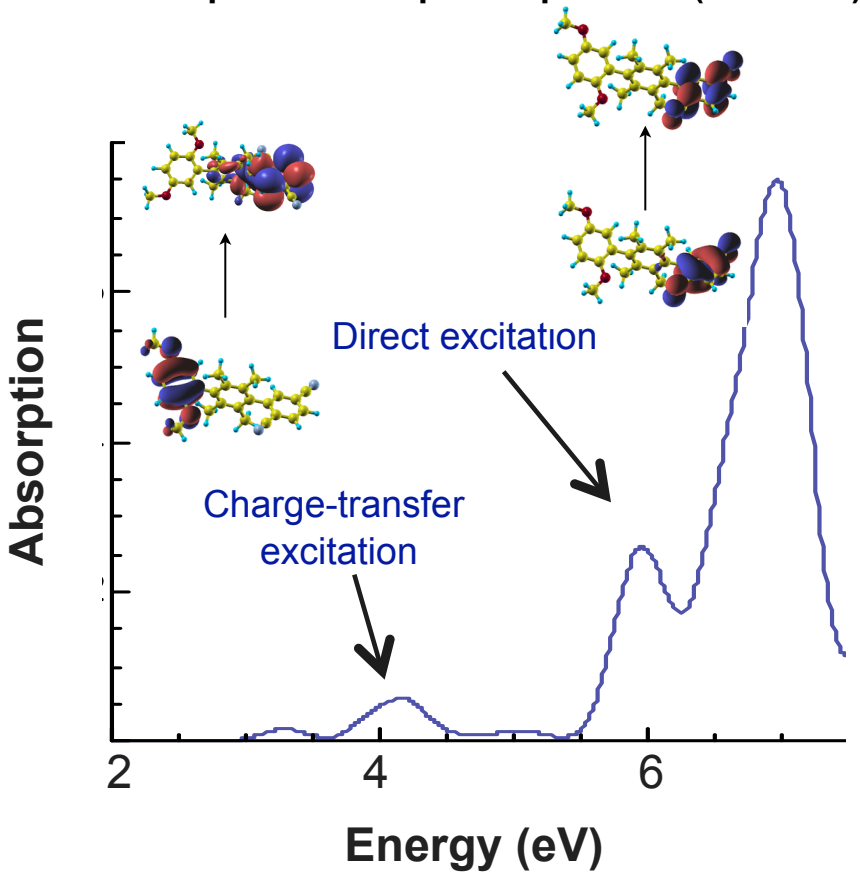
Light-Matter Interactions at Organic-Organic Nanoscale Interfaces

Bipolar Molecules w/ Charge Transfer Excited States



w/ Don Tilley (UCB, via Helios)

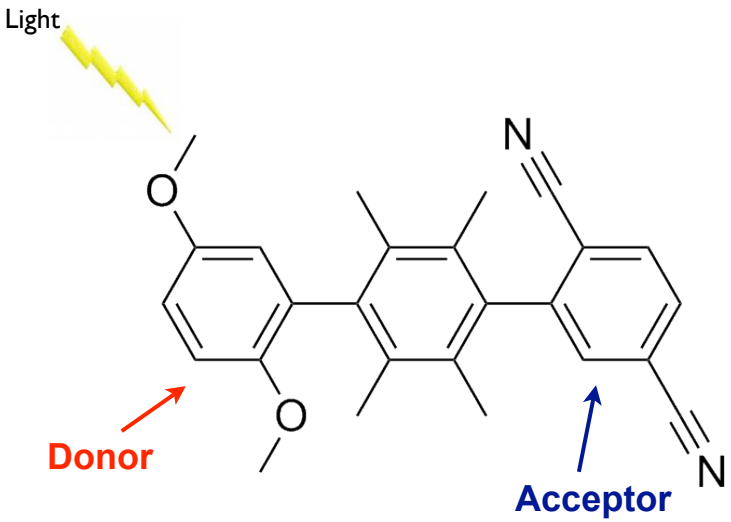
Computed Absorption Spectrum (GW-BSE)



- Realistic model systems for understanding fundamental mechanisms in PV (absorption, excitons, charge separation)
- What about charge injection & dynamics?

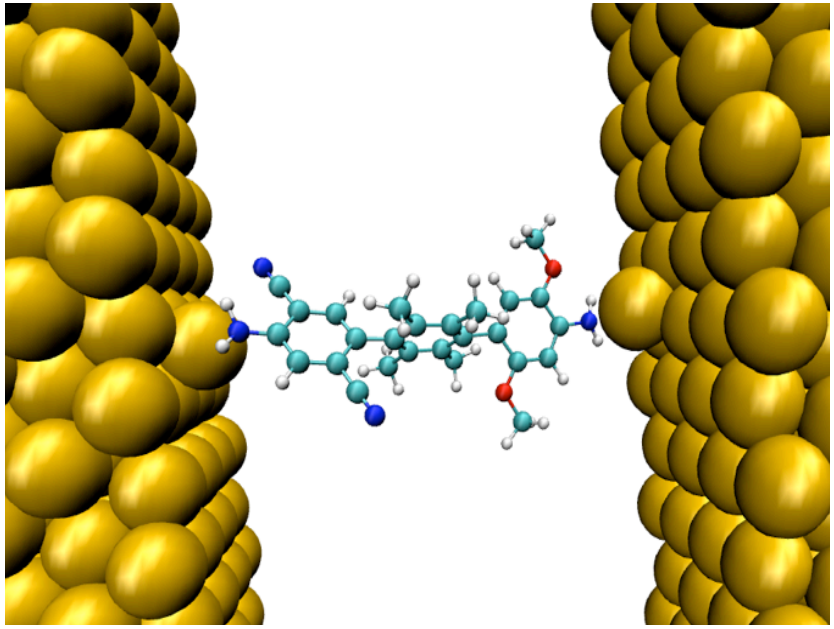
Future: Light-Matter Interactions w/ Interfaces

Bipolar Molecules w/ Charge Transfer Excited States



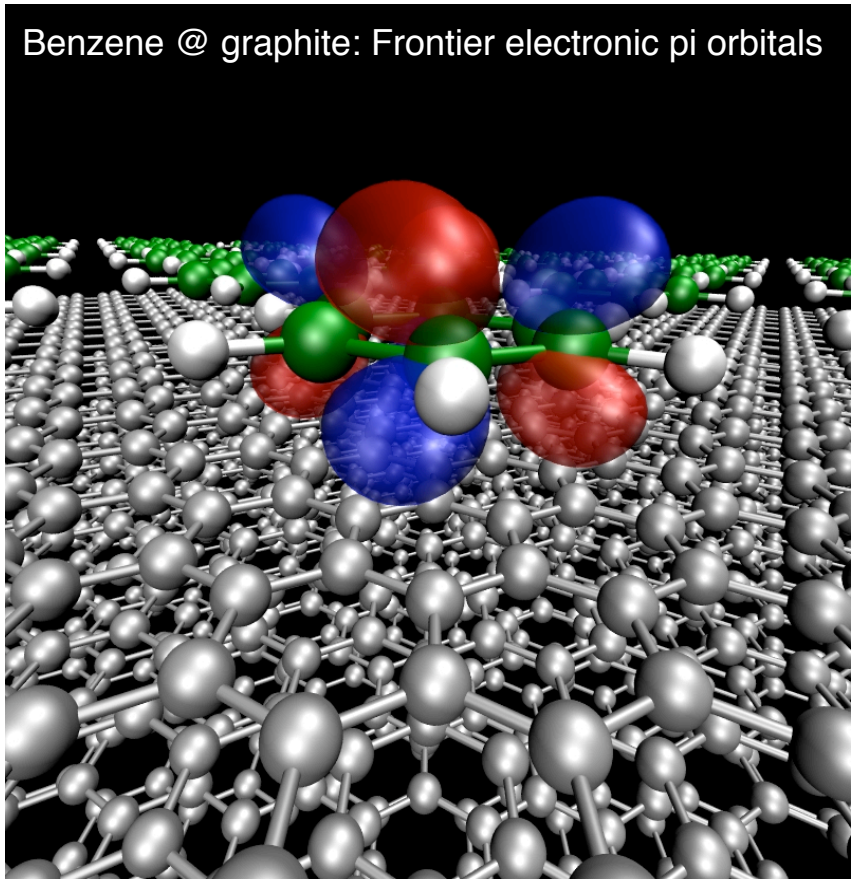
w/ Don Tilley (UCB, via Helios)

Conductance, photocurrent, and IV characteristics in Bipolar Molecular Junctions

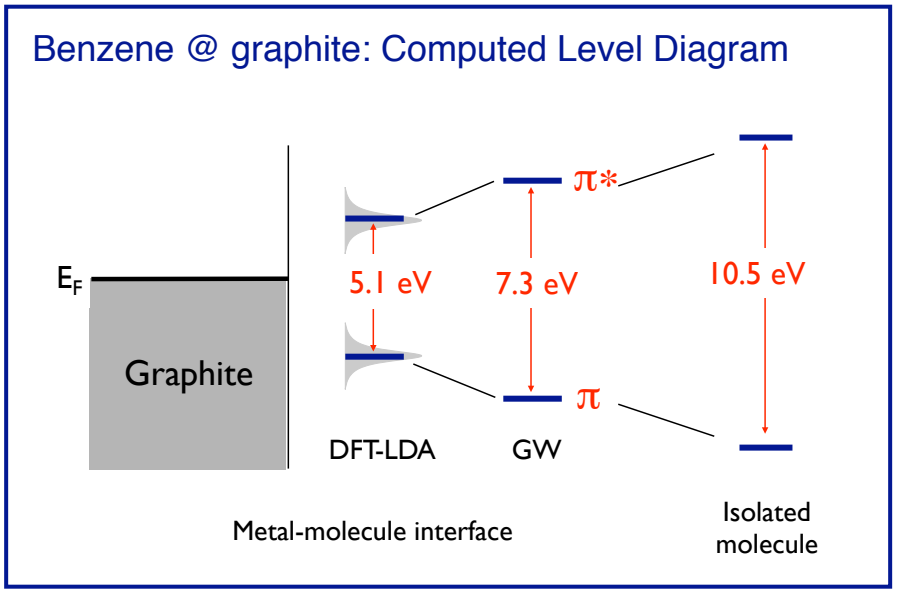


- Excited states, conductance, photocurrent generation, etc

Excited States Strongly Altered at Metal-Organic Interfaces

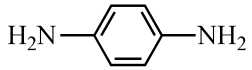


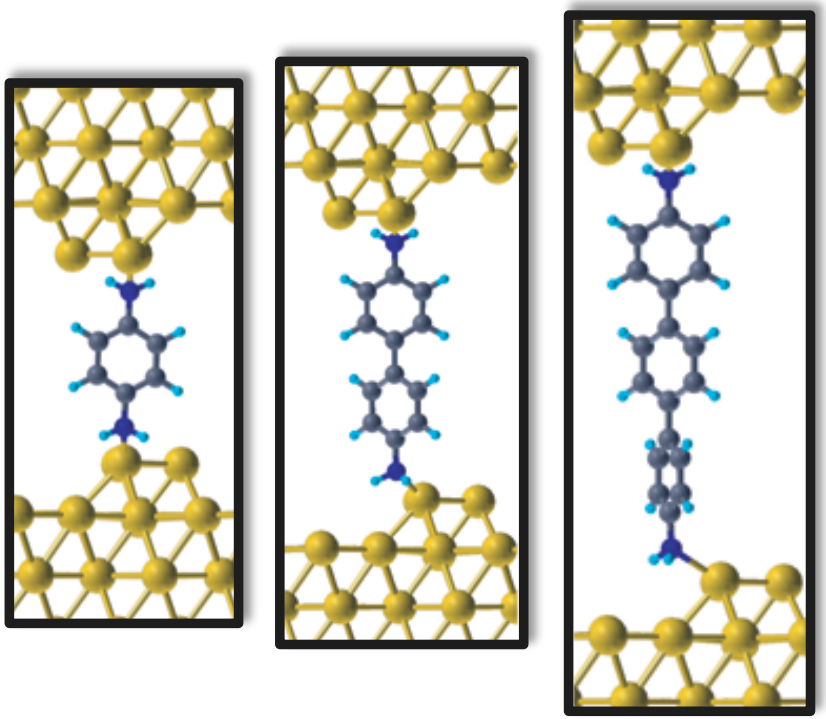
Neaton, Hybertsen, Louie, Phys. Rev. Lett. **97**, 216405 (2006)

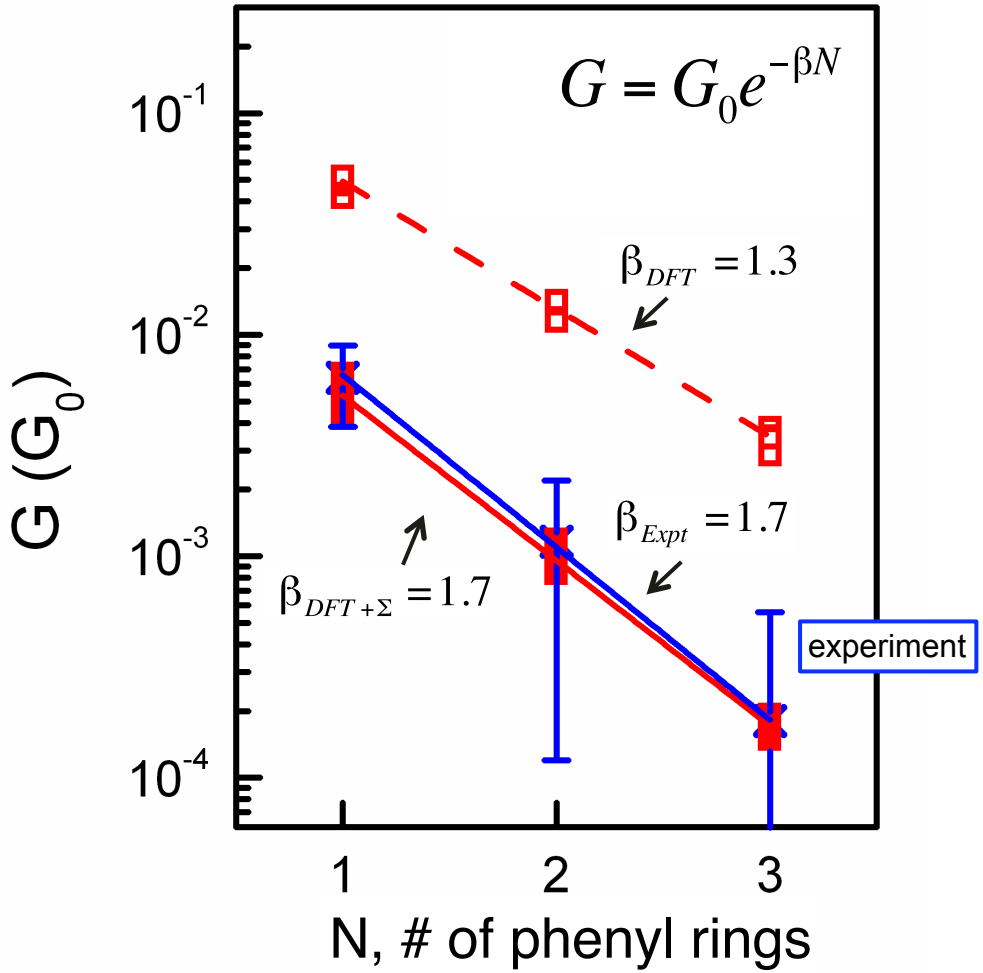


- Nonlocal electronic correlations between the molecule and substrate (static polarization) reduce HOMO-LUMO gap
- Simple 'image' charge model accounts for nearly all of the reduction
- Paves the way for a new approach to quantum transport

Length Dependence of Molecular Junction Conductance: Quantitative Agreement w/ Expt

Phenyl amines 

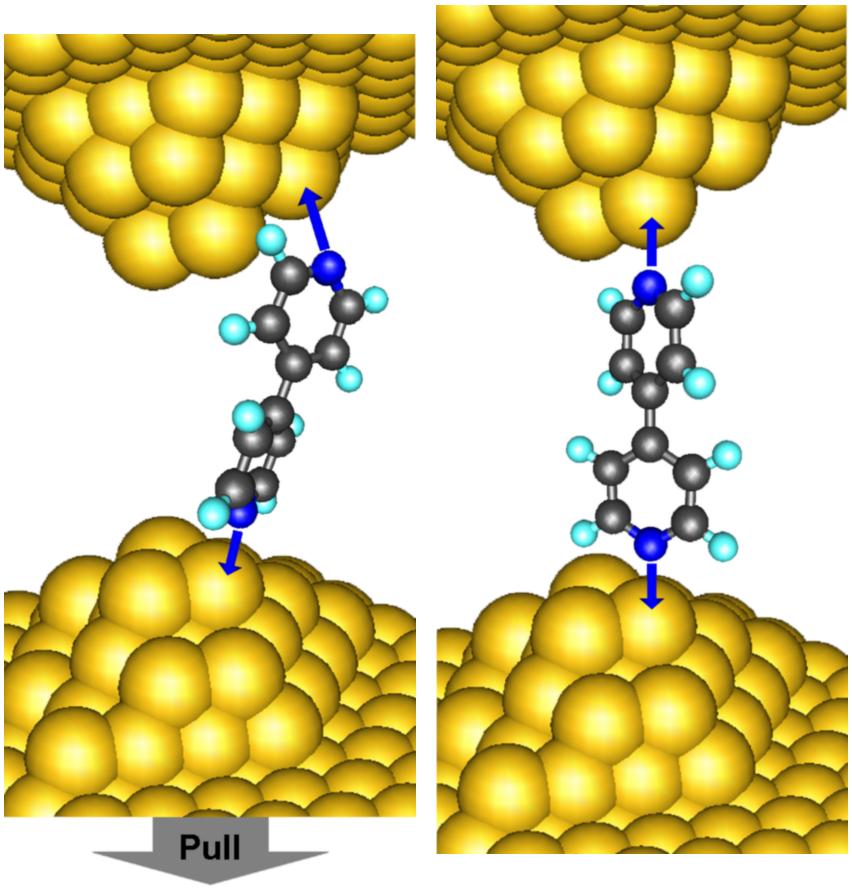




User/Internal Research

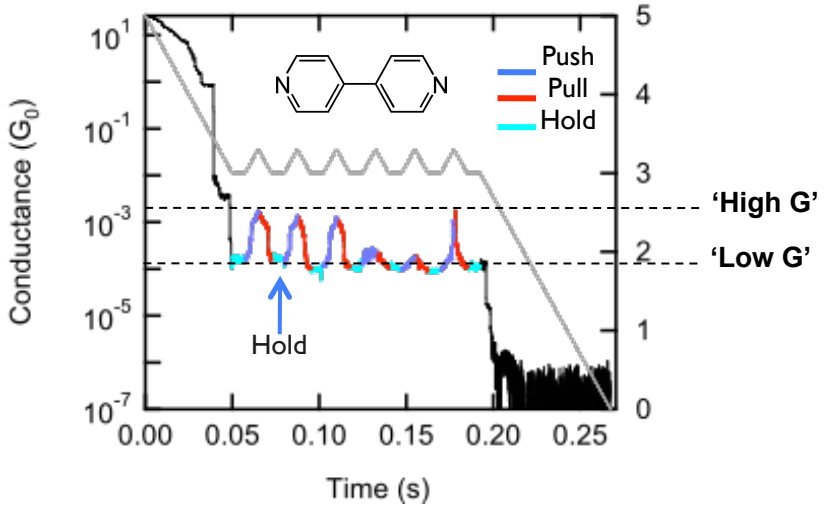
Quek et al, Nano Lett. **7**, 3477 (2007);
Quek et al, Nano Lett, **9**, 3949 (2009)

Mechanically-Controlled Binary Switching of a Molecular Junction



DFT-based calculations explain recent experiments reporting mechanically-controlled conductance switching in a molecular junction.

Measured Single-Molecule Switching Trace



Working with experimentalists for validation of methods and approximations will continue to be important

Quek et al, Nature Nanotechnology **4**, 230 (2009)

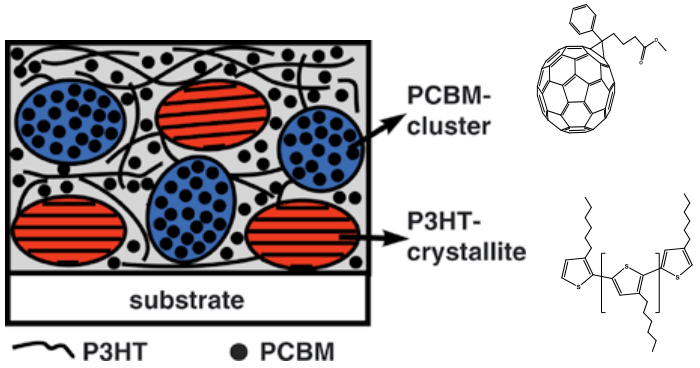
3-5 Years & Beyond

- Future: Access excited states for 300-500+ atom systems will require 10x more resources
- Continued support for 2GB/core
- High bandwidth, low latency interconnects
- Large scratch (>0.5TB), rapid access to HPSS
- High throughput for jobs of 1000s of cores, several hours
- New algorithm developments remove unoccupied subspace, but will largely scale the same way

  Umari et al, arXiv:0910.0791
  Giustino et al, cond-mat/arXiv:0912.3087
- Need for more approximate, effective schemes
- Web-based interfaces

Morphology & Excited States

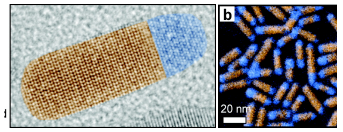
Multicomponent Organic Systems



Erb et al., *Adv. Funct. Mater.* **15**, 1193 (2005)

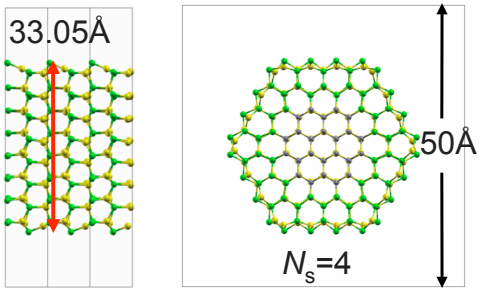
Multicomponent Inorganic Systems

CdS/Ag_2S



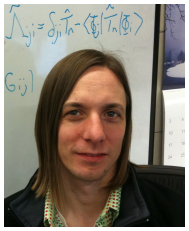
Sadtler et al, *JACS* **131**, 5285 (2009)

$(CdSe)_2/(CdTe)_2$ core/shell



Web-based Interfaces for Training (and research?)

http://nanohub.org/

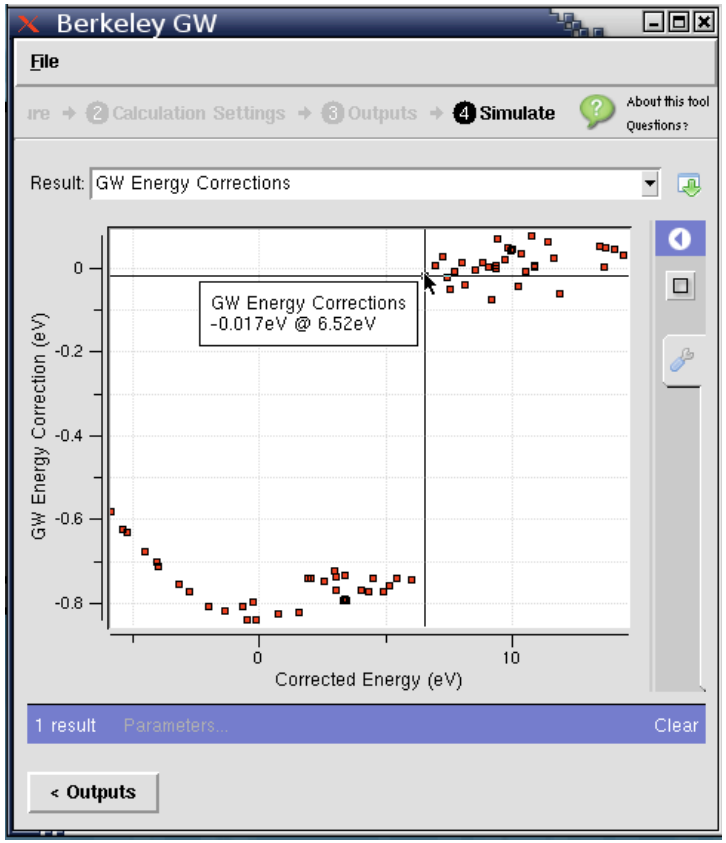


Peter Doak



S. Sharifzadeh

- Understanding excited and computing excited state properties is crucial for treatment of photovoltaics dynamics:
  - » Molecular level alignment
  - » Excited state charge transfer
- New tool presents the GW approximation formalism for calculating electronic excited states in solids and molecular systems.
- Based on a series of DFT calculations, followed by a multi-body perturbation theory calculation to obtain energy and structure corrections.

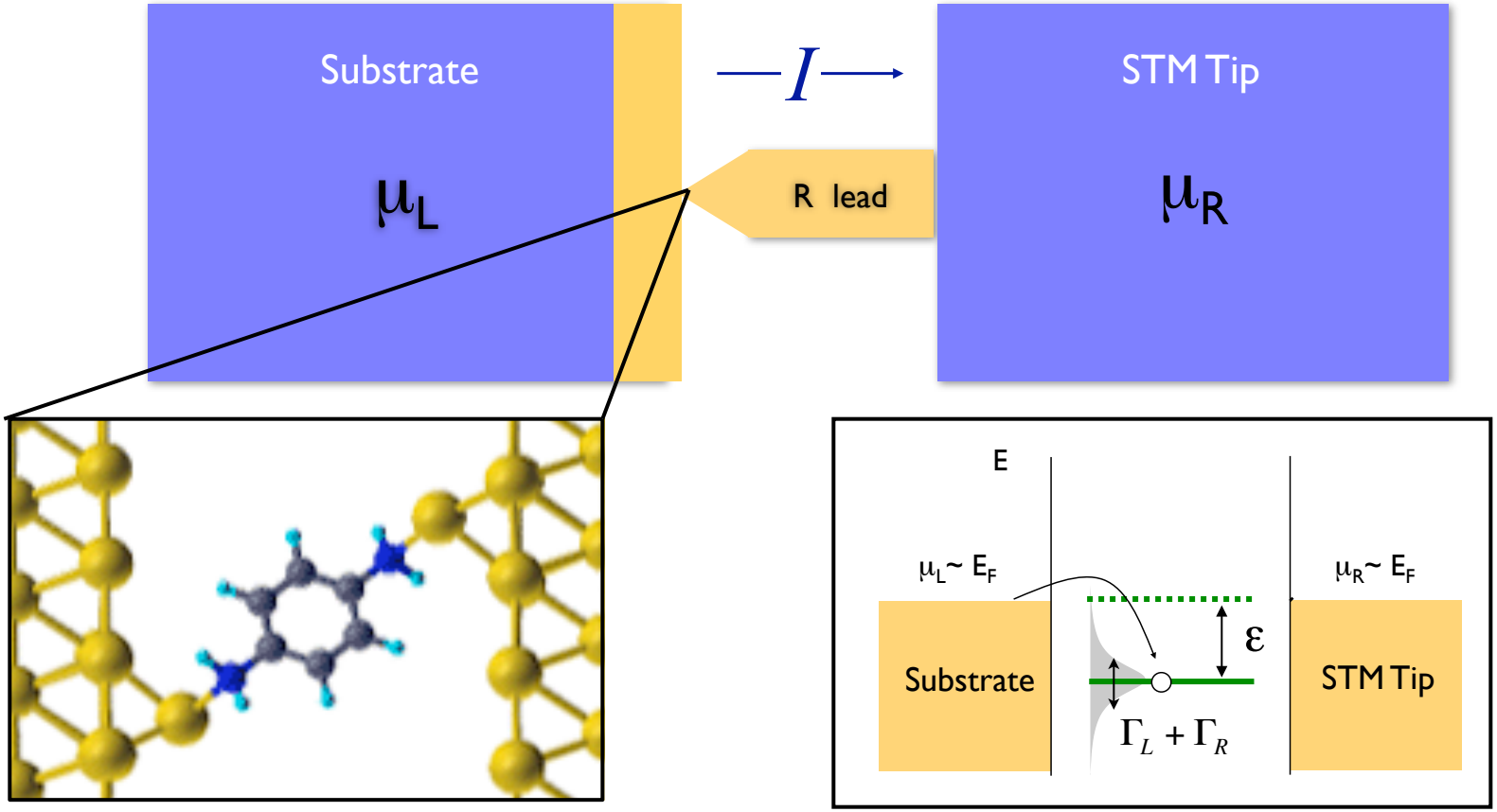


BerkeleyGW

If time permits...

details of quantum transport methods

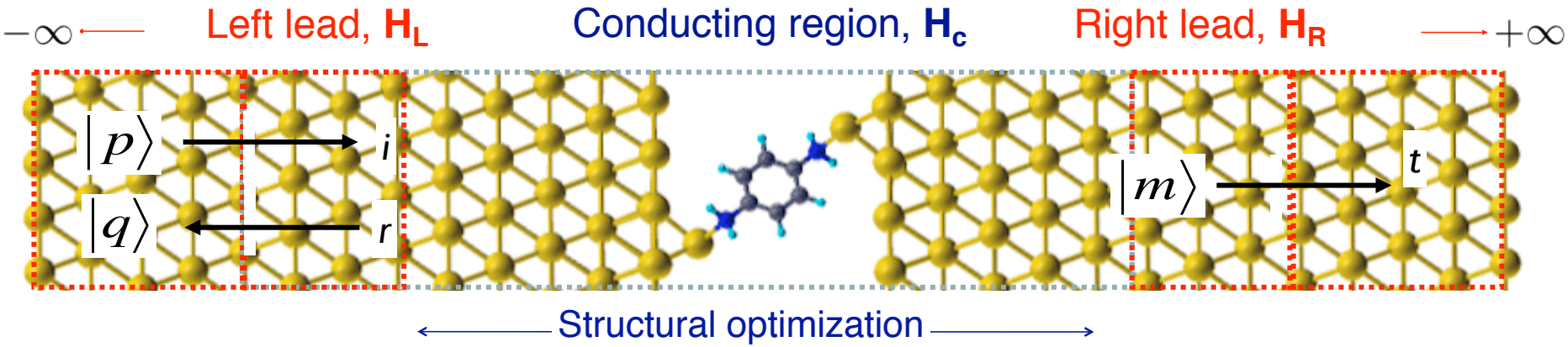
First-Principles Electronic Transport: Geometry & Interfacial Level Alignment



Landauer Conductance within DFT

$$\frac{\delta I}{\delta V} \rightarrow \frac{2e^2}{h}\mathrm{Tr}[\Gamma_L G_C^r \Gamma_R G_C^a] = \frac{2e^2}{h}T(E_F)$$

Scattering-state approach



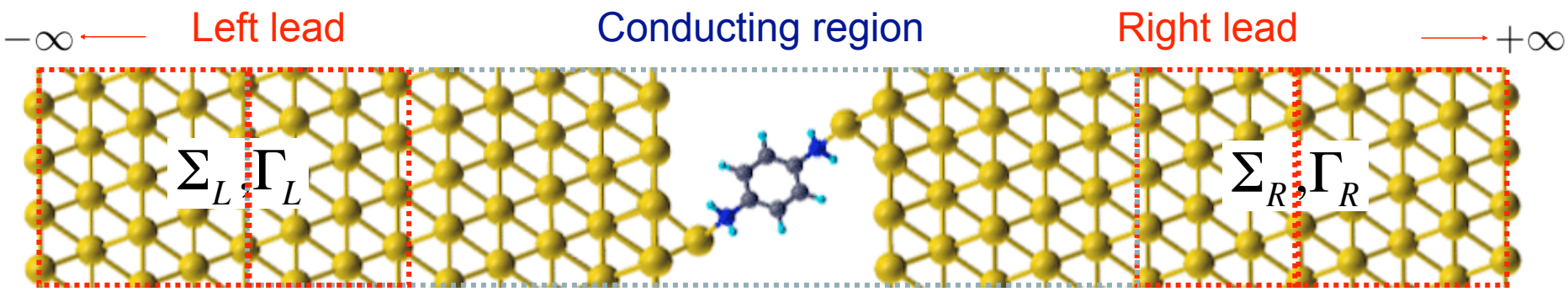
- Density functional theory (DFT-PBE) with a local-orbital basis (SIESTA)
- Coherent scattering (SCARLET) H. J. Choi et al, Phys. Rev. B **76**, 155420 (2007)
- Scattering-state wavefunctions

$$\left|\psi_p^L(E_p, k_{//,p})\right\rangle = |p\rangle + \sum_q r_{pq}|q\rangle + \sum_m t_{pm}|m\rangle + \sum_l c_{pl}|l\rangle$$

- Conductance from transmission (Landauer formula)

$$G = \frac{2e^2}{h}T(E_F) \equiv T(E_F)G_0 \quad \text{where} \quad T(E) = Tr(t^\dagger t),\ t = t_{pm}(E)$$

Green's function approach



$$G_C = (\varepsilon S_C - H_C - \Sigma_L - \Sigma_R)^{-1}$$

Green's function of conductor

$$\Gamma_{\{L,R\}} = i[\Sigma^r_{\{L,R\}} - \Sigma^a_{\{L,R\}}]$$

Couples conductor & leads

Zero-bias conductance
(mean-field)

$$\left.\frac{dI}{dV}\right|_{V\to 0} = \frac{2e^2}{\hbar}\mathrm{Tr}(\Gamma_L G^r_C \Gamma_R G^a_C)$$

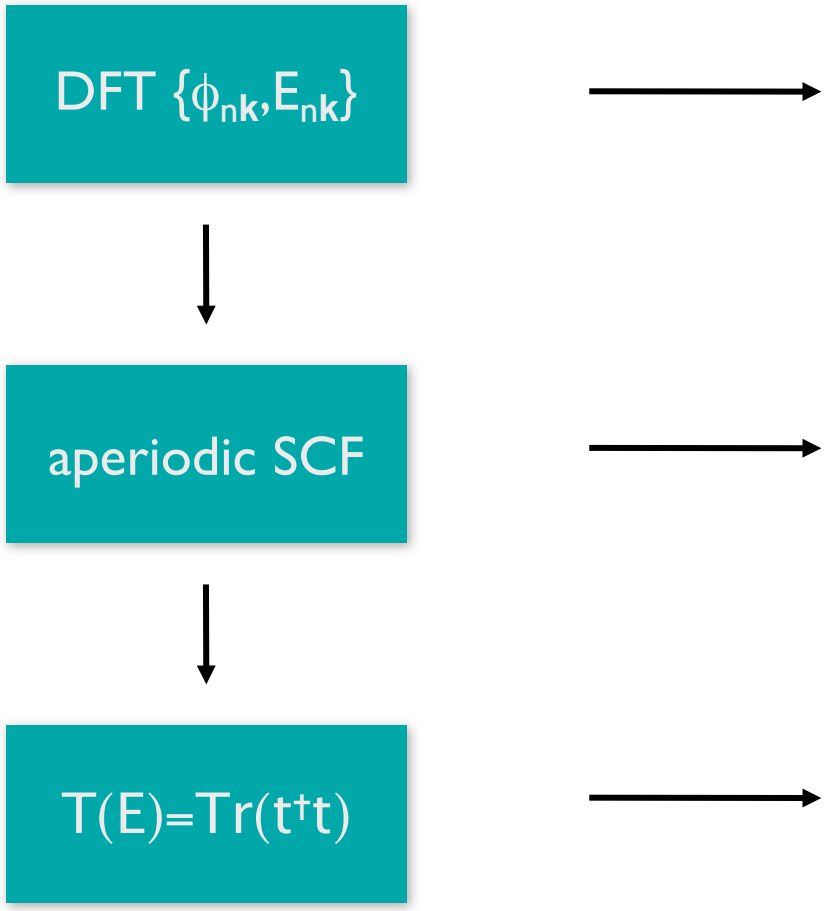
Meir, Wingreen (1992)
Datta (1995)

Taylor, Guo, & Wang, Phys. Rev. B **63**, 245407 (2001)
Damle, Ghosh, & Datta, Phys. Rev. B **64**, 201403 (2001)
Brandbyge et al, Phys. Rev. B **65**, 165401 (2002)
Xue, Datta, & Ratner, Chem. Phys. **281**, 151 (2002)

Other approaches

Hirose et al, Phys. Rev. B **69** 245412 (2004)
Lang, Phys. Rev. B 52, 5335 (1995)
Di Ventra, Pantelides, Lang, Phys. Rev. B **65**, 045402 (2002)

SCARLET Implementation & Scaling



- SCF for ground-state (Siesta LCAO, NC-PPs)
- **Bottleneck:** Lots of atoms (~600), iterative diagonalization

- SCF for with fixed Hartree potential deep in the leads (Siesta LCAO, NC-PPs)
- If finite bias, need scattering states on dense energy grid between the two chemical potentials
- **Bottleneck:** Lots of atoms (~600), iterative diagonalization, LU decomposition at many energies

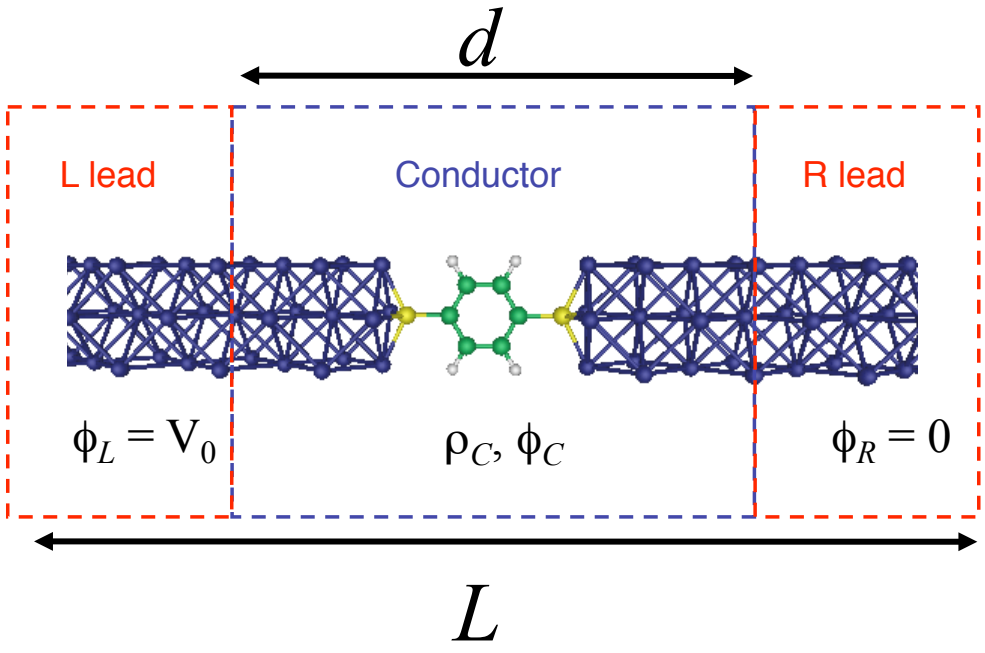
- Generate transmission function
- LU decomposition at 100-1000's of energies
- **Bottleneck:** LU decomposition. Trivially parallel over energy.

Modified Poisson solver

Given ρ_C, solve

$$\nabla^2 \phi_C = 4\pi\rho_C$$

for fixed bias V_0



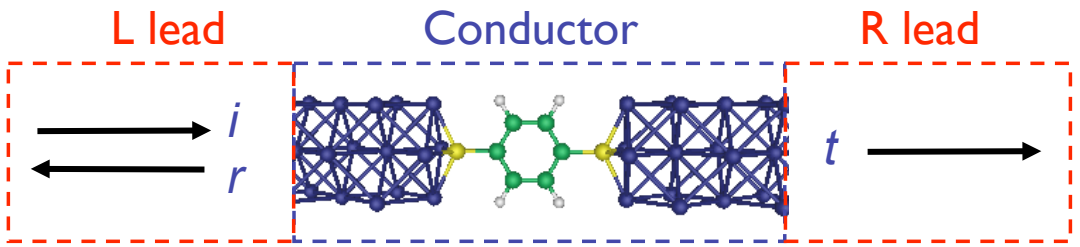
1. Obtain ϕ in Conductor using periodic boundary conditions $\phi_C(z) = \phi_C(z+L)$
2. Match ϕ_C with ϕ_L and ϕ_R at boundaries using homogenous solution satisfying
3. $\nabla^2 \phi_C^0 = 0$ solved without FFT (N_{grid}^2 scaling) with $\phi(z) - \phi(z+d) = V_0$

Need to adapt a more efficient solver for arbitrary boundary conditions

Scattering state solutions

Problem Solve **A**(E)X = Y(E) for the vector of coefficients X, where **A** is an N x N matrix (~70% zero elements)

Physical geometry & boundary conditions



Wavefunction vector

$$\left|\Psi_L(E)\right\rangle = \left[1, X\right] = \left[1 \quad t_1 \ldots t_{N_c} \quad r_1 \ldots r_{N_c} \quad c_1 \ldots c_{N_o}\right]$$

2 sets of N_c coefficients (propagating & evanescent waves)

1 set of N_o coefficients (total number of orbitals in basis set)

dim X = $N = N_o + N_c \sim 10^3$

- X = $\mathbf{A}^{-1}$Y scales as N^3
- Ideally, we use ~10^3 energies

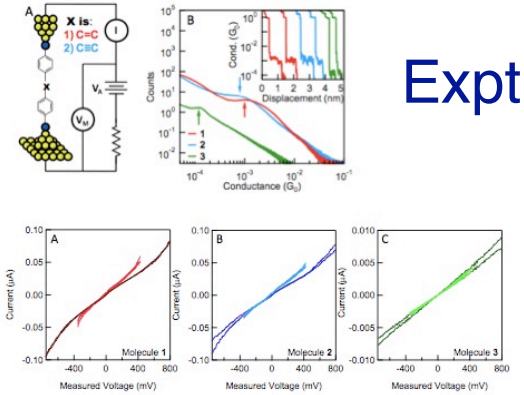
Need for efficient matrix inversion routines

3-5 Years & Beyond

- Finite bias calcuations, improved treatment of correlation, nonequilibrium effects
- Continued support for 2GB/core
- High bandwidth, low latency interconnects
- Large scratch (>0.5TB), rapid access to HPSS
- High throughput for jobs of 1000s of cores, several hours
- New algorithm developments remove unoccupied subspace, but will largely scale the same way
- Need for more approximate, effective schemes

Transport: Finite bias & Excited States

Expt



J. R. Widawsky, et al, Nanotechnology, in press (2009)

Theory

