Life Beyond DFT:
Computational methods for electron correlations, excitations, and tunneling transport

Guest lecturer:
Jeff Neaton, Molecular Foundry, LBNL
Examples of Applications

Silicon Nanowires

Carbon Nanotubes

Single-molecule junctions
Nanoscale materials: What’s different

• Large fraction of surfaces, interfaces

• Quantum confinement

• Strong electron-electron & electron-hole interactions

• Ballistic & resonant charge transport

• Every atom counts …
Density Functional Theory

Energy $\rightarrow$ Electron density

\[ E_0 = E[n_0] \]

Hohenberg & Kohn, 1964

\[ G = E + pV - TS \]

Structure, dynamics, vibrational properties
Good for covalently-bonded solids
(LDA, GGA not so good for van der Waals interactions)
Density Functional Theory

Interacting $\rightarrow$ Non-interacting

$$\left( -\frac{1}{2} \nabla^2 + V^H + V^{xc} + V^{ext} \right) \phi_i(r) = \varepsilon_i \phi_i(r)$$

Kohn & Sham, 1965

Wavefunctions

Band structures
Interpretation of the Kohn-Sham system

• In DFT, the Kohn-Sham (KS) orbitals are a means to an end: they provide a route for obtaining the charge density and total energy.

• The KS eigenvalues are Lagrange multipliers introduced to ensure the orbitals are orthogonal.

• Strictly speaking, neither the KS orbitals nor eigenvalues have physical significance.

• However, for the exact functional, the maximum occupied KS eigenvalue equals the ionization potential:

\[ \varepsilon_{\text{max}}^{KS} = -IP \]

GW corrects DFT excitation energies

**Band gaps**

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GWA (a)</th>
<th>Exp</th>
</tr>
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<tbody>
<tr>
<td>diamond</td>
<td>3.9</td>
<td>5.6</td>
<td>5.48</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.52</td>
<td>1.29</td>
<td>1.17</td>
</tr>
<tr>
<td>Germanium</td>
<td>~0</td>
<td>0.75</td>
<td>0.74</td>
</tr>
<tr>
<td>LiC</td>
<td>6.0</td>
<td>9.1</td>
<td>9.4</td>
</tr>
</tbody>
</table>

GW improves on the DFT gap problem

**Fig. 2.** (Color online) PBE and quasiparticle energies $G_0W_0$ and $GW_0$. Logarithmic scale is used for both axes.


Hybertsen and Louie, 1986
Optical absorption spectrum of bulk Si

\[ \varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_{\nu c} |\vec{\lambda} \cdot \langle \nu | \nu \rangle|^2 \delta(\omega - (E_c - E_\nu)) \]

Courtesy of Steven Louie
Optical absorption spectrum of bulk Si

\[ \varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_{vc} |\vec{\lambda} \cdot \langle \vec{v} | \vec{c} \rangle|^2 \delta(\omega - (E_c - E_v)) \]

Courtesy of Steven Louie
Optical absorption spectrum of Si

Optical absorption spectrum of Si

Optical absorption spectrum of Si

Outline

• **Quasiparticle excitations**: GW ‘self-energy’
• **Optical excitations**: Bethe-Salpeter equation
• **Charge transport**: Landauer formula
Mind the gap

Quasiparticle gap (charged excitation)

• Electron addition & removal
  e.g., band structure, HOMO-LUMO gaps of molecules
  – Photoemission & inverse photoemission (PES, ARPES)
  – Scanning tunneling microscopy (STM)
  – Band offsets, Schottky barriers
  – Charge injection

Optical gap (neutral excitation)

• Electron transitions between occupied & empty states
  e.g., absorption spectra, $\varepsilon_2(\omega)$
  – Optical absorption
  – Fluorescence/photoluminescence
  – Pump-probe experiments
Quasiparticle gap

Electron addition/removal

$E_g = IP - AE$

Ionization energy

$IP = E(N - 1) - E(N)$

Electron affinity

$EA = E(N + 1) - E(N)$

Jeff Neaton, Molecular Foundry, LBNL
Physical interpretation of quasiparticles

- Excitations of many-electron system can often be described in terms of weakly interacting “quasiparticles”

- Quasiparticle (QP) = bare particle + polarization clouds

\[ E_{QP} = E^0 + \Sigma \]

\( \Sigma \): response of system to the excitation (self-energy)
Similarities to the Kohn-Sham equation

Schrödinger-like equation for quasiparticles

\[ (-\frac{1}{2} \nabla^2 + V^0) \phi_i(x) + \int \Sigma(x,x',\varepsilon_i) \phi_i(x') dx' = \varepsilon_i \phi_i(x) \]

Schrödinger-like Kohn-Sham equation

\[ (-\frac{1}{2} \nabla^2 + V^H + V^{xc} + V^{ext}) \phi_i(r) = \varepsilon_i \phi_i(r) \]

Where the self-energy is independent of \( \varepsilon_i \) and has the form

\[ \Sigma(x,x';\varepsilon_i) = V^{xc}(x') \delta(x - x') \]
Quasiparticle energies are computed to first order as

\[ E_{n\mathbf{k}}^{QP} = E_{n\mathbf{k}}^{LDA} + \langle n\mathbf{k} | \Sigma(E_{n\mathbf{k}}^{QP}) | n\mathbf{k} \rangle - \langle n\mathbf{k} | V_{xc}^{LDA} | n\mathbf{k} \rangle \]

where the self-energy operator \( \Sigma \) is approximated as

\[ \Sigma = iG_0W = iG_0\varepsilon^{-1}V \]

and \( G \) is constructed from Kohn-Sham eigenvalues & eigenstates (independent particle \( G \))

\[ G = \sum \frac{\phi_{nk}(r)\phi_{nk}^*(r')}{E - \varepsilon_{nk}} \]
GW Implementation

DFT \{\phi_{nk}, E_{nk}\}  
\rightarrow

RPA \epsilon^{-1}(q,0)  
\rightarrow

\Sigma = iGW  
\rightarrow

- PARATEC code
- SCF for ground-state (PW, NC-PPs)
- NSCF for 100’s of empty states

- xi0 code
- Computes \chi_0(q) for G, G’
- Inverts for \epsilon^{-1}(q) for each G, G’

- sigma code
- Forms matrix elements to compute \Sigma, including GPP
- Outputs \Sigma - V_{xc} for specified nk
GW calculations for H-terminated Si nanowires

\[ E_g = E_{g,\text{bulk}} + \text{const} \times \left( \frac{1}{d} \right)^\alpha \]

\[ \alpha = 1.7 \]

- Good agreement with STM expts
- Corrections are diameter-dependent

Total optical gap = Electron addition/removal – exciton binding energy

\[ E_g = IP - AE - E_{e-h} \]

\[ E_{e-h} \sim -\frac{e^2}{\varepsilon 2a_0} \]

Approx.
Neutral (electron-hole) excitations

Im part of the transverse dielectric function

$$\varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_s |M|^2 \delta(\omega - \Omega_S)$$

Optical gap ➔ Two-particle Green’s function

$$G(1,2,1',2') = (-i)^2 \langle N | T\{\psi(1)\psi(2)\psi^+(2')\psi^+(1')\} | N \rangle$$
Bethe-Salpeter equation (BSE)

Seek two particle solutions of the form

$$|S\rangle = \sum_{vck} A^{S}_{vck} |vc\krangle$$

where $|vc\krangle$ is taken as the product of occupied & empty quasiparticle states (Tamm-Dancoff approximation).

Bethe-Salpeter equation

$$(E_{ck} - E_{vk}) A^{S}_{vck} + \sum_{v'c'k'} \langle vck | K^{eh} | v'c'k' \rangle A^{S}_{v'c'k'} = \Omega^{S} A^{S}_{vck}$$

where $\Omega_{S}$ is the excitation energy of the state S
Optical absorption spectra

Imaginary part of the transverse dielectric function:

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

\[ \vec{\lambda} = \frac{A}{\overline{A}} \]

\[ \vec{v} = i/\hbar [H, \vec{r}] \]

Same thing, without electron-hole interactions:

\[ \varepsilon_2(\omega) = \frac{16\pi e^2}{\omega^2} \sum_{vc} \left| \vec{\lambda} \cdot \langle v | \vec{v} | c \rangle \right|^2 \delta(\omega - (E_c - E_v)) \]
Optical absorption spectra, cont’d

BSE optical transition matrix elements:

\[ \langle 0 | \overline{v} | S \rangle = \sum_{\nu} \sum_{\ell} A_{\nu \ell}^S \langle \nu | \overline{v} | \ell \rangle \]

Coherent sum of matrix elements of contributing electron-hole transitions.
- Spectrum dominated by bona fide and resonant excitons
- Large binding energies ~ 1 eV!

Other approaches

- Hybrid functionals (e.g. B3LYP) and exact exchange (EXX)
  - Includes only GGA correlation
  - Static & dynamic polarization-response physics missing from HF self-energy

- Self-interaction correction (SIC) & LDA+U
  - Ad hoc, though SIC less so (only in projection scheme)
  - esp. LDA+U for heterogeneous systems, interfaces, etc (where U is tough to define)

- Time-dependent density functional theory (TD-DFT)
  - Exact theory in principle for neutral excitations, but no quasiparticles
  - In practice, adiabatic LDA is OK for molecules, poor for solids
Other approaches, cont’d

• **Quantum Monte Carlo (QMC)**
  – Accurate ground-state approach; excited-states require good ansatz trial wavefunction

• **Many-body quantum chemistry (coupled-cluster, MP2, etc)**
  – Accurate, but can scale poorly & is prohibitive for solids

• **DFT total energy differences (ΔSCF)**
  – Can be reasonably accurate for frontier quasiparticle levels, but difficult to obtain full excitation spectrum

• **Dynamical mean-field theory (DMFT)**
  – Successful for systems with large local moments (d-, f-metals)
System of Interest: Molecular or nanostructure sandwiched between two leads

Landauer Formula:

\[ G = \left. \frac{\delta I}{\delta V} \right|_{V \to 0} = \frac{2e^2}{h} \times \text{Number of channels} \rightarrow \frac{2e^2}{h} T(E_F) \]
Single-molecule measurement w/ statistics

- Break & reform atomic point-contacts with a modified scanning-probe setup

- Measure conductance on breaking, repeat $\sim 10^4$ times, collect statistics

Xu and Tao, Science (2003)
Single-molecule measurement w/ statistics

**Molecular hydrogen-(Pt,Pd)**

- H<sub>2</sub> peak $\rightarrow$ 1 $G_0$
- Pt peak $\rightarrow$ 1.5 $G_0$

Number of Counts

<table>
<thead>
<tr>
<th>Conductance ($G_0$)</th>
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<tbody>
<tr>
<td>0</td>
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<tr>
<td>0.0064</td>
</tr>
<tr>
<td>0.01</td>
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<tr>
<td>0.1</td>
</tr>
</tbody>
</table>

Counts


**Benzene dithiol-Au**

- 0.01 $G_0$ ± ~50%

Conductance (1.1x10^{-2}$G_0$)

Counts


**Alkane chains (e.g. hexane-dithiol)-Au**

- 0.00036 $G_0$ ± ~50%

Conductance (10^{-9}$G_0$)

Counts


**Benzene diamine-Au**

- 0.0064 $G_0$ ± 40%

Conductance ($G_0$)

Scattering-state approach

- Density functional theory (DFT-PBE) with a local-orbital basis (SIESTA)
- Coherent elastic scattering
  - Choi et. al., PRB 76, 155420 (2007)
- Scattering-state wavefunctions

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

- 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

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

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

\[ \frac{dI}{dV} \bigg|_{V \to 0} = \frac{2e^2}{\hbar} \text{Tr}(\Gamma_L G_C^r \Gamma_R G_C^a) \]

Zero-bias conductance (mean-field)

Other approaches


Meir, Wingreen (1992)
Datta (1995)
Example: Weakly-coupled level

Single level coupled to metal continuum

\[ G_C = (E - H - \Sigma)^{-1} = (E - \varepsilon_0 - i\Gamma)^{-1} \]

Simple Lorentzian Transmission \( T(E) \)

\[ \frac{dI}{dV}_{V \to 0} = \frac{2e^2}{\hbar} T(E) = \frac{2e^2}{\hbar} \text{Tr}(\Gamma_L G \Gamma_R G) \]

\[ = \frac{2e^2}{\hbar} \frac{\Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)^2 + (E_F - \varepsilon_0)^2} \]
Typical zero-bias transmission spectrum

Transmission vs. Energy (eV)

$T(E_F) = 0.046$

Level alignment at metal-molecule contacts

Physical effects
- Interfacial charge transfer (dipoles)
- Quantum mechanical (electronic) coupling
- Surface polarization
Model Self-Energy Correction to DFT HOMO

**DFT-GGA**

- HOMO
- LUMO
- LUMO + 1

\[ T(E_F) = 0.046 \]

\[ G_{\text{theory}} = 0.046 \, G_0 \pm 33\% \]

\[ G_{\text{expt}} = 0.0064 \, G_0 \pm 40\% \]

\[ G_{\text{DFT+corr}} = 0.007 \, G_0 \]

**DFT + Model self-energies**

- Static polarization response \( \sim 1 \, \text{eV} \)
- Self-energy correction in gas phase \( \sim -3 \, \text{eV} \)

\[ 0.046G_0 \, (\text{GGA}) \]

\[ 0.007G_0 \, \text{Corrected} \]

\[ 0.0064G_0 \, (\text{expt}) \]

- DFT-GGA distribution agrees well with expts
- Model electron correlation correction explains difference between theory & expt

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Quek et al, Nano Letters 7, 3477 (2007)

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Comparison with experiment: Amines & Pyridines

Calculated Conductance ($G_0$) vs Experimental Conductance ($G_0$)

- DFT-GGA (vertical geometries)

Jeff Neaton, Molecular Foundry, LBNL
Comparison with Experiment: Amines & Pyridines

Calculated Conductance ($G_0$) vs. Experimental Conductance ($G_0$)

- DFT-GGA (vertical geometries)
- DFT + self-energy corrections

Quek et al, unpublished (2008)