GW approach to quantum transport in nanocontacts

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Outline

- DFT-based transport calculations – brief overview
- Basic idea of a GW-based transport scheme

- Formalism (NEGF)
- The non-equilibrium GW equations
- Anderson model and Kondo effect

- Wannier-GW implementation
- Hydrogen molecule between Pt chains
- Conclusions and outlook
Landauer-Büttiker/NEGF combined with DFT:

- Coherent transport (no correlation, no inelastic scattering)
- Kohn-Sham effective potential (LDA,GGA)
- Pseudopotentials
- Various basis sets (Real-space, LCAO,Gaussians,Wannier functions, wavelets)
- Self-consistent bias
- Leads and molecule treated on an equal footing.
DFT-based transport calculations

Applications:

- Junctions with small chemisorbed molecules (Pt/Au with H2 / CO)
- Metallic point contacts / atomic wires
- Contacts with larger organic molecules linked via S or N groups
  [Calculated conductance up to $10^3 \times$ experimental value!]

Physical effects:

- Interference effects (conductance fluctuations, even-odd effects)
- Charge transfer, non-equilibrium charge redistribution
- Correlation effects (Coulomb blockade, Kondo effect)
- Inelastic effects (el-ph coupling)

Lee et al. PRB 69, 125409 (2004)
J. Reichert et. al PRL 88, 176804 (2002)
Beyond DFT – \( GW \) in molecular region

**Basic assumption:**
Electrodes can be described by effective Hamiltonian (Fermi-liquid theory)
Correlation effects only important in molecular region

\[
\Sigma_{int}(\omega) = \begin{pmatrix} V_{xc} & V_{xc} & V_{xc} \\ V_{xc} & \Sigma_{GW}(\omega) & V_{xc} \\ V_{xc} & V_{xc} & V_{xc} \end{pmatrix}
\]

**Why \( GW \)?**
\( GW \) improves LDA quasi-particle band structures.
Self-interaction free.
Simplest non-trivial approximation beyond HF.
The Hamiltonian:

\[ \hat{H}(t) = \hat{h}(t) + \hat{V} \]

Non-interacting part (assuming localized basis):

\[ \hat{h}(t) = \begin{pmatrix} h_{LL} & 0 & 0 \\ 0 & h_{CC} & 0 \\ 0 & 0 & h_{RR} \end{pmatrix} + \theta(t - t_0) \begin{pmatrix} 0 & h_{LC} & 0 \\ h_{CL} & 0 & h_{CR} \\ 0 & h_{RC} & 0 \end{pmatrix} \]

Interactions in central region:

\[ \hat{V} = \sum_{i,j,k,l \in C} V_{i,j,k,l} \hat{C}_{i\sigma}^{\dagger} \hat{C}_{j\sigma'}^{\dagger} \hat{C}_{l\sigma'} \hat{C}_{k\sigma} \approx \sum_{i,j,\sigma,\sigma'} \tilde{V}_{i\sigma,j\sigma'} \hat{C}_{i\sigma}^{\dagger} \hat{C}_{j\sigma'}^{\dagger} \hat{C}_{j\sigma'} \hat{C}_{i\sigma} \]
Initial conditions

At times $t < t_0$ the three regions are decoupled, each being in thermal equilibrium with its own heat bath.

Equilibrium state of the left lead:

$$\hat{\varrho}_L = \frac{1}{Z_L} \exp(-\beta(\hat{h}_L - \mu_L \hat{N}_L))$$

$$Z_L = \text{Tr}[\exp(-\beta(\hat{h}_L - \mu_L \hat{N}_L))]$$

The initial state (equilibrium at times $t < t_0$):

$$\hat{\varrho} = \hat{\varrho}_L \hat{\varrho}_C \hat{\varrho}_R$$
The retarded GF of the central region:

\[
G^r_C(\omega) = \left[ (\omega + i\eta) I_C - h_C - \Sigma_L^r(\omega) - \Sigma_R^r(\omega) - \Sigma^r(\omega) \right]^{-1}
\]

Correlation functions:

\[
G^{<\!\!/\!\!>} = G^r_C \Sigma_{tot}^{<\!\!/\!\!>} G_C^{\alpha}(\omega) + \Delta^{<\!\!/\!\!>}
\]

Current from lead $\alpha$ into central region:

\[
I_\alpha = \int \frac{d\omega}{2\pi} \text{Tr} \left[ \Sigma^{<\!\!/\!\!>}(\omega) G^>(\omega) - \Sigma^>(\omega) G^{<\!\!/\!\!>}(\omega) \right]
\]

Symmetrized current:

\[
I = \frac{i}{4\pi} \int \text{Tr} \left[ (\Gamma_L - \Gamma_R) G^{<\!\!/\!\!>} + (f_L \Gamma_L - f_R \Gamma_R) (G^r_C - G^{\alpha}_C) \right] d\omega
\]
Non-equilibrium GW equations

$$\sum_{GW} = \begin{array}{c}
\text{Wickled line: Truncated interaction} \\
\text{Straight line: GF of coupled central region}
\end{array}$$

\begin{align*}
\Sigma_{GW,ij}(\tau, \tau') &= iG_{ij}(\tau, \tau') W_{ij}(\tau, \tau') \\
W_{ij}(\tau, \tau') &= \tilde{V}_{ij} \delta_C(\tau, \tau') \\
&\quad + \sum_{kl} \int_C d\tau_1 \tilde{V}_{ik} P_{kl} \delta_C(\tau_1, \tau_1) W_{lj}(\tau_1, \tau') \\
P_{ij}(\tau, \tau') &= -iG_{ij}(\tau, \tau') G_{ji}(\tau', \tau).
\end{align*}

On the Keldysh contour:

In real time:

\begin{align*}
\Sigma_{GW,ij}^r(t) &= iG_{ij}^r(t) W_{ij}^>(t) + iG_{ij}^< t W_{ij}^>(t) \\
\Sigma_{GW,ij}^{</>(t)} &= iG_{ij}^{</>(t)} W_{ij}^{</>(t)}, \\
W^r(\omega) &= \tilde{V} [I - P^r(\omega) \tilde{V}]^{-1} \\
W^{</>(\omega)} &= W^r(\omega) P^{</>(\omega)} W^a(\omega) \\
P_{ij}^r(t) &= -iG_{ij}^r(t) G_{ji}^r(-t) - iG_{ij}^< t G_{ji}^a(-t) \\
P_{ij}^{</>(t)} &= -iG_{ij}^{</>(t)} G_{ji}^>(-t).
\end{align*}

- All quantities represented on frequency/time grid.
- FFT is used to avoid convolutions.
Anderson model

\[ \varepsilon_0 \quad \quad t_0 \quad \quad U \quad \quad \varepsilon_c \quad \quad t_c \]

Spin-dependent interaction:

\[ \hat{V} = \begin{pmatrix} 0 & U \\ U & 0 \end{pmatrix} \]

The Kondo regime:

\[ \varepsilon_c / \Gamma \ll -0.5 \]

Kondo temperature:

\[ T_K = \frac{\sqrt{U \Gamma}}{2} \exp \left( \frac{\pi \varepsilon_c (\varepsilon_c + U)}{\Gamma U} \right) \]

Calculated DOS at central site:

\[ \text{Im } G(\omega) \quad \text{(arb. units)} \]

-5 -4 -3 -2 -1 0 1 2

\[ \omega - E_F \]
• Side peaks are due to the level crossing the edges of the bias window.

• $GW$ conductance drops sharply as $V$ is raised from 0. (No splitting of Kondo resonance observed)

• $G_0W_0$ shows unphysical behavior (negative differential conductance) due to its non-conserving nature

• Violation of current conservation increases with bias and is not present in linear response regime
The Kohn-Sham Hamiltonian:

\[ \hat{h}_s = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \]

Localized Wannier functions:

\[ \phi_i(\mathbf{r}) = \sum_j U_{ji} \psi_j(\mathbf{r}) \]

- Orthogonal, maximally localized
- Span all states below \( E_{\text{cut}} \)
- Include states above \( E_{\text{cut}} \) if this can further improve localization.

The Dacapo code:
- Plane-wave basis
- Supercells
- Pseudopotentials (ultrasoft)

Extend by bulk lead potential

KS matrix elements and Coulomb integrals:

\[ \hat{h}_s = \begin{pmatrix} h_{LL} & h_{LC} & 0 \\ h_{CL} & h_{CC} & h_{CR} \\ 0 & h_{RC} & h_{RR} \end{pmatrix} \]

\[ V_{ijkl} = \int \int \text{d}r \text{d}r' \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \phi_k(\mathbf{r}) \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \]
Partially occupied Wannier functions

Band disentanglement for poly-acetylene:

Bonding-antibonding closure for isolated benzene:
- Restores symmetry of pi-system
- Improves localization

Wannier-GW implementation #2

\[ G^r = \left[ (g^r_s)^{-1} + v_{xc} + \sum_h^r [g^{(eq)}_s] - \sum_h^r [G] - \sum_{GW}^r [G] \right]^{-1} \]

Subtract xc-potential to avoid double counting

GW self-energy

KS Green function of the coupled system

Correction to DFT Hartree potential coming from finite bias and correlations.

\[ g^r_s = \left[ (\omega + i\eta)I - h_s - \sum_L^r - \sum_R^r \right]^{-1} \]

Truncated interactions: \( V^{(1)} \) is used for Hartree and exchange, \( V^{(2)} \) is used for correlation.

\[ \hat{V}^{(1)} = \hat{V}[\{V_{i,j,i,j}\}, \{V_{i,j,j,i}\}] \]
\[ \hat{V}^{(2)} = \hat{V}[\{V_{i,j,i,j}\}, \{V_{i,j,j,i}\}, \{V_{i,i,j}\}, \{V_{i,j,i}\}, \{V_{i,j,i,j}\}, \{V_{j,i,j}\}] \]
**Hydrogen molecule between Pt chains**

**DFT(PW91):**
- Bonding state is a bound state at -7 (relative to $E_F$).
- Anti-bonding state close to 0, but strongly broadened by coupling to Pt

**SCHF (in central region):**
- Bonding state shifted to -16.
- Anti-bonding state only shifted little due to increase in Hartree energy (4 eV).
Hydrogen molecule between Pt chains

Large difference between the two $G_0W_0$ results!

The quasi-particle energy of bonding state:

$$
\varepsilon_{QP} = \varepsilon_{HF}(G_0) + \varepsilon_{corr}(G_0)
$$

Increases by 5 eV when going from $G_{DFT}$ to $G_{HF}$ because of increase in Hartree energy.
Conclusions & outlook

- Non-equilibrium $GW$ in the central region/non-interacting leads has been studied.
- Self-consistency is important to satisfy continuity equation.
- One-shot $GW$ calculations leads to unphysical results at finite bias.
- Combination with DFT and Wannier function basis for application to real nanocontacts.

- More efficient implementation/storing scheme
- Larger basis set
- Larger central region
Isolated $\text{H}_2$

<table>
<thead>
<tr>
<th>State</th>
<th>$E_{\text{PW91}}$</th>
<th>$V_{xc}$</th>
<th>$\Sigma_x$</th>
<th>HF</th>
<th>$G_0W_0$</th>
<th>GW</th>
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</thead>
<tbody>
<tr>
<td>HOMO ($\sigma$)</td>
<td>-10.3</td>
<td>-11.2</td>
<td>-17.3</td>
<td>-16.3</td>
<td>-15.8</td>
<td>-16.1</td>
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<tr>
<td>LUMO ($\sigma^*$)</td>
<td>0.4</td>
<td>-2.1</td>
<td>-0.6</td>
<td>1.9</td>
<td>1.8</td>
<td>1.9</td>
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</tbody>
</table>

(This method)

<table>
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<tr>
<th>State</th>
<th>$E_{\text{PBE}}$</th>
<th>CC</th>
<th>HF</th>
<th>$G_0W_0(\text{LDA})$</th>
<th>GW</th>
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<tbody>
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<td>HOMO ($\sigma$)</td>
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<td>-15.9</td>
<td>-16.1</td>
<td>-15.92</td>
<td>-16.22</td>
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<td>LUMO ($\sigma^*$)</td>
<td>0.2</td>
<td>1.7</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
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(NIST Chemistry WebBook database+preprint by A. Stan, N. E. Dahlen and R. Van Leeuwen)