Coherent electronic transport in nanostructures and beyond

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Acknowledgments

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Outline

- Motivations

- The method
  
  *Ab initio* electronic transport from max. loc. Wannier Functions:
  
  - Development
  - Implementation (*WanT code*)
  - Application to nanoscale systems

- Inclusion of correlation in transport
  
  Application to short range e-e interaction regime
Novel systems for electronic devices (nanotubes, atomic chains, molecular systems,...)

Semiclassical transport theory breaks down

Full quantum mechanical approach → Landauer Theory
**Ballistic transport**

- **Ballistic transport**: exclusion of non-coherent effects (e.g. dissipative scattering or e-e correlation).

- **Quantum conductance**: depends on the local properties of the conductor (transmission - scattering) and the distribution function of the reservoirs

\[
G = \frac{2e^2}{h} T(E_f)
\]

- **Landauer Formula**

- **Transmittance from real-space Green’s functions techniques**

\[
T(E) = \text{Tr} \{ \Gamma_L G_C^r \Gamma_R G_C^a \}
\]

- **Fisher & Lee formulation**

- **Need for a localized basis set**
The “WanT” approach

♦ Create a connection between
  ♦ *ab initio* description of the electronic structure by means of state-of-the-art DFT-plane wave calculations
  ♦ Real space Green’s function techniques for the calculation of quantum conductance.

♦ Idea: Unitary transformation of delocalized Bloch-states into

Maximally localized Wannier functions

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WanT method

Wannier functions (WFs): definition

Single band transformation:

$$|n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{R}} |\psi_{n\mathbf{k}}\rangle$$

Generalized transformation:

$$|n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{R}} \sum_m U_{mn}^{(k)} |\psi_{m\mathbf{k}}\rangle$$

Non-uniqueness of WFs under gauge transformation $U_{mn}^{(k)}$

Goal: Calculation of WFs with the narrowest spatial distribution

Maximally localized Wannier functions*

Wannier functions: localization

\[ \langle r^2 \rangle_n = \langle R_n | r^2 | R_n \rangle \]
\[ \langle r \rangle_n = \langle R_n | r | R_n \rangle \]

**Spread functional**

\[ \Omega [U] = \sum_n \left[ \langle r^2 \rangle_n - \langle r \rangle_n^2 \right] \]

**Maximal localization** given by the minimization of the **spread** wrt \( U \):

\[ \frac{\delta \Omega [U]}{\delta U^k} = 0 \]

**WF advantages:**
- orthonormality
- completeness
- minimal basis set
- adaptability
- direct link to phys. prop.

**WF disadvantages:**
- no analytical form
- computational cost
- algorithm stability
Flow diagram

- **DFT**
  - Conductor (supercell)
  - Leads (principal layer)

- **WFs**

- **GFs**
  - All quantities on Wannier basis

- **QC**
  - Zero bias
  - Linear response

Quantum conductance
WanT Code

Features:

- Input from PW-PP, DFT codes.
- Maximally localized Wannier Functions computation.
- Transport properties within a matrix GF’s Landauer approach.
- GNU-GPL distributed
Zigzag (5,0) carbon nanotube with a substitutional Si defect

- Si polarizes the WF’s in its vicinity affecting the electronic and transport properties of the system
- General reduction of conductance due to the backscattering at the defective site
- Characteristic features (dips) of conductance of nanotubes with defects

A. Calzolari et al., PRB 69, 035108 (2004).
Beyond the coherent regime
Correlated transport in nanojunctions

♦ Evidences of strong e-e correlation effects:
  ♦ Kondo effect
  ♦ Coulomb blockade


♦ Goal: Ab initio description of electronic transport in the presence of strong electron-electron coupling, from atomistic point of view.*

♦ Landauer formalism breaks down:

Need for a novel theoretical treatment

* A. Ferretti et al., PRL 94, 116802 (2005)
Re-formulate the theory from more general conditions: Meir-Wingreen approach

\[ I = \frac{e}{2\hbar} \int d\omega \text{Tr} \left\{ [\Sigma_L^\leq - \Sigma_R^\leq] [G_C^r - G_C^a] + i [\Gamma_L - \Gamma_R] G_C^\leq \right\} \]

**Generalized Landauer-like formula**

\[ I = \frac{e}{\hbar} \int \frac{d\omega}{2\pi} \left[ f_L - f_R \right] \text{Tr} \left\{ \Gamma_L G_C^{rrr} \Gamma_R \Lambda G_C^{a} \right\} \]

**Effective transmittance**

A. Ferretti et al., PRL 94, 116802 (2005)

**Correlated transport** → **Landauer + e-e correction to the Green’s functions**

- Conductor GF’s are interacting
- Lambda is also given by:
  \[ \Lambda = 1 + \left[ \Gamma_L + \Gamma_R + 2\delta^+ \right]^{-1} \Gamma_{corr} \]
Correlation effects:

- **Three Body Scattering (3BS) method**
- Describes the **strong short range** electron-electron interaction
- Based on a configuration interaction scheme up to **3 interacting bodies** (1 particle + 1 e-h pair) of the generalized Hubbard Hamiltonian
- Hubbard U is an adjustable parameter

*F. Manghi, V. Bellini and K. Arcangeli, PRB 56, 7159 (1997).*
Flow diagram

DFT

Conductor (supercell) Leads (principal layer)

Atomic pdos

3BS

Correlation

$\Sigma_{nn'k}(\omega)$

WFs

Mean field

GFs

All quantities on Wannier basis

QC

Quantum conductance

All quantities on Wannier basis
Correlated Pt chain

Transport components
- C coherent comp.
- I incoherent comp.
- T total

quasi-particle
finite lifetimes

3 correlated atoms

![Graph showing transmittance vs energy with N=1,2,4 and N=3 labeled.]
Nanotubes: Co impurity

- **EXP**: Cobalt impurities adsorbed on metallic CNT

  \[ \text{Work in progress} \]

- **THEO**: Co @ 5,0 CTN

  \[ \text{T.W. Odom et al., Science 290, 1549 (2000)} \]

  - Transition metal (TM) often present as catalysts
  - Interplay between CNT and TM physics
  - Changes on electronic and transport properties

  \[ \text{Work in progress} \]
Conclusions and outlook

- Development of the freely available WanT (Wannier-Transport) code.

- Inclusion of electron correlation (incoherent, non-dissipative model), in the strong short-range regime (by 3BS method).

- Application to Pt chains:
  - Renormalization effects on quantum transmittance and conductance
  - Importance of finite QP lifetimes
DFT calc.  
PW basis  
WFs determination  
Stability issues with hundreds of WFs  

Transport calc.  
Wannier functions basis

Strategies:
- Existing code optimization
- PAW / USPP implementation
- Variational functional redefinition, minimization procedure

\[ |R_n\rangle = \frac{V}{(2\pi)^3} \int dke^{-i\mathbf{k} \cdot \mathbf{R}}|\psi_{nk}\rangle \]

\[ \Omega = \sum_n \left[ \langle r^2 \rangle_n - \bar{r}^2_n \right] \]
Molecular nanostructures


- Co coordination complex
- Prototype for correlation effects in molecular electronics
- Computationally challenging

Free molecule

Device configuration

Work in progress
Correlation within LDA+U

3 correlated atoms

Static coherent description
Pt@Au chain

3 correlated atoms

- Au chain
- Mean field Pt@Au
- Correlated Pt@Au

Interface effects do not suppress correlation

Transmittance vs. Energy [eV]

(b) Pt@Au
**Hypotheses:**
Leads are non-interacting
The problem is stationary

**Definitions:**
Using a localized basis set:

\[
H = \sum_{l' \in LR} H_{ll'} c_l^{\dagger} c_{l'} + H_{\text{int}}(\{d_i^\dagger\}\{d_j\}) + \sum_{l \in LR \atop i \in C} \left[ H_{li} c_i^{\dagger} d_i + H_{il} d_i^{\dagger} c_i \right]
\]

\[
H_0 = \begin{bmatrix}
H_{LL} & H_{LC} & 0 \\
H_{CL} & H_{CC} & H_{CR} \\
0 & H_{RC} & H_{RR}
\end{bmatrix}
\]

\[
G(\omega) = \begin{bmatrix}
G_{LL} & G_{LC} & G_{LR} \\
G_{CL} & G_{CC} & G_{CR} \\
G_{RL} & G_{RC} & G_{RR}
\end{bmatrix}
\]

Operators in block matrix form
Coupling to the leads

**Leads self-energies**

- From the block inversion of the hamiltonian
- Allows to treat the coupling to the leads
- Computational interest

\[
\Sigma^r_L(\omega) = H_{CL} \ g^r_{LL}(\omega) \ H_{LC}
\]

\[
\Sigma^a_L(\omega) = H_{CL} \ g^a_{LL}(\omega) \ H_{LC}
\]

\[
\Gamma_L(\omega) = i \ [\Sigma^r_L(\omega) - \Sigma^a_L(\omega)]
\]
Expression for the current

*Exact expression from Meir & Wingreen*

\[ I = \frac{e}{2\hbar} \int d\omega \ Tr \left\{ [\Sigma^<_L - \Sigma^<_R] [G^r_C - G^a_C] + i [\Gamma_L - \Gamma_R] G^<_C \right\} \]

**In the interacting case**

Ng-ansatz for \( G^{\leq,\geq} \)

\[ \Sigma^<(\omega) = \Sigma^<_0(\omega) \Lambda(\omega) \]
\[ \Sigma^>(\omega) = \Sigma^>_0(\omega) \Lambda(\omega) \]

Which results in

\[ \Lambda = \left[ \Sigma^r_0 - \Sigma^a_0 \right]^{-1} \left[ \Sigma^r - \Sigma^a \right] \]

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N. Sergueev et al., PRB 65, 165303 (2002)
Equilibrium Green Functions

Various definitions:

Time ordered

\[ G(1, 2) = -i \langle T \left[ \psi(1), \psi^\dagger(2) \right] \rangle \]

Correlation functions

\[ G^<(1, 2) = i \langle \psi^\dagger(2) \psi(1) \rangle \]
\[ G^>(1, 2) = -i \langle \psi(1) \psi^\dagger(2) \rangle \]

Retarded, Advanced

\[ G^r(1, 2) = \theta(t_2 - t_1) [G^<(1, 2) - G^>(1, 2)] \]
\[ G^a(1, 2) = \theta(t_1 - t_2) [G^>(1, 2) - G^<(1, 2)] \]

Allows perturbation theory (Wick’s theorem)

Direct access to observable expectation values

Simple analytical structure and spectral analysis
Analitycal properties

### Time ordered GF

- **Retarded GF**
  - $\text{Re } \omega$
  - $\text{Im } \omega$

- **Advanced GF**
  - $\text{Re } \omega$
  - $\text{Im } \omega$

**Fermi Energy = 0.0**
Equilibrium Green Functions

\( G^r, G^a, G^<, G^> \) are enough to evaluate all the GF’s and are connected by physical relations

\[
G^r(\omega) - G^a(\omega) = G^>(\omega) - G^<(\omega)
\]

General identity

\[
G^a(\omega) = G^{r\dagger}(\omega)
\]

Fluctuation-dissipation th.

\[
G^<(\omega) = i f_{eq}(\omega) A(\omega)
\]

Spectral function

\[
A(\omega) = i [G^r(\omega) - G^a(\omega)]
\]

➢ Just one independent GF
Non-Equilibrium GF’s

- Electric fields (TD laser pulses)
- Coupling to contacts at different chemical potentials

**Contour-ordered perturbation theory:**

$G^r$, $G^a$, $G^<$, $G^>$ are all involved in the PT

2 of them are independent

Only the identity holds
(no FD theorem)

\[ G^r(1, 2) - G^a(1, 2) = G^>(1, 2) - G^<(1, 2) \]
In the time-independent limit

➢ Two Equations of Motion

\[
G^r(\omega) = G_0^r + G_0^r \Sigma^r(\omega) G^r(\omega) \quad \text{Dyson Equation}
\]

\[
G^< = [1 + G^r \Sigma^r] G_0^< [1 + \Sigma^a G^a] + G^r \Sigma^< G^a \quad \text{Keldysh Equation}
\]

\( G^r, G^< \) coupled via the self-energies

Computing the (coupled) \( G^r, G^< \) allows for the evaluation of transport properties