Conductance Calculations for Small Molecules

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Outline

• Framework – Density Functional Theory
• Conductance calculations – methodology
• Examples:
  – $\text{H}_2$/Pt
  – CO/Pt
  – Bipyridine/Au
  – Nitrobenzene/polyacetylene/Au
Conductance Calculations

Landauer Büttiker setup:
- One electron picture
- Phase coherent electrons
- All scattering takes place in S (periodic leads)
- Semi-infinite leads

The electron potential:
- Plane-wave pseudopotential DFT code (Dacapo)
- Supercell of "extended S"
- Separate calculation for lead potential

Density Functional Theory

- Ground state energetics – in principle exact.
- The success of approximations based on experience. (Problems with correlations, van der Waals, ...)
- Kohn-Sham potential constructed to reproduce electron density with non-interacting electrons.
- Is not meant for excitation spectra – but (static) charge transfer should be well described.
- Attitude: Let us see how far we can go. Try simple explanations first.
- Starting point for further developments: Time-dependent DFT, GW, ...
One Electron Picture

• Exactly solvable model (with many names)
  - Newns-Anderson model
  - U=0 Anderson model
  - Fano-Anderson model
  - The resonant level model

• Useful for chemisorption, resonant tunneling, ...

• Can be extended with Hubbard U (Anderson model), phonon-coupling, ...
Density of states projected onto adsorbate site:

\[
\rho_a(\varepsilon) = \frac{1}{\pi} \frac{\Delta(\varepsilon)}{(\varepsilon - \varepsilon_a - \Lambda(\varepsilon))^2 + \Delta(\varepsilon)^2}
\]

\[
\Delta(\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k)
\]

coupling-weighted density of states

\[
\Lambda(\varepsilon) = \frac{1}{\pi} P \int d\varepsilon' \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'}
\]

Hilbert transform
Wide Band System

\[ \epsilon_k \]
\[ |k\rangle \]
\[ \Delta_0 \]
\[ |a\rangle \]

\[ \Delta(\epsilon) = \pi \sum_k |V_{ak}|^2 \delta(\epsilon - \epsilon_k) = \Delta_0 \]

\[ \Lambda(\epsilon) = \frac{1}{\pi} P \int d\epsilon' \frac{\Delta(\epsilon')}{\epsilon - \epsilon'} = 0 \]

\[ \rho_a(\epsilon) = \frac{1}{\pi} \frac{\Delta_0}{(\epsilon - \epsilon_a)^2 + \Delta_0^2} \]
Two Level System

\[ \Delta(\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k) = |V|^2 \delta(\varepsilon - \varepsilon_k) \]

\[ \Lambda(\varepsilon) = \frac{1}{\pi} P \int d\varepsilon' \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} = \frac{1}{\pi} |V|^2 \frac{1}{\varepsilon - \varepsilon_k} \]

\[ \rho_a(\varepsilon) = a_+ \delta(\varepsilon - \varepsilon_+) + a_- \delta(\varepsilon - \varepsilon_-) \]
Semi-elliptical bands

Weak coupling

Strong coupling

antibonding

bonding
Oxygen adsorption on transition metals

- Metal $d$-projected DOS
- Oxygen $\sigma$-projected DOS

Graphs showing the DOS for different transition metals:
- Ni
- Ca
- Ru
- Pd
- Ag
- Pt
- Au

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Fine-tuning reactivity:

For a fixed local geometry:

Correlation between adsorption energies and activation barriers and the d-band center

Mavrikakis, Hammer, Nørskov
The Group Orbital

\[ |g\rangle = N (\hat{H} |a\rangle - \varepsilon_a |a\rangle) = N \left( \sum_k V_{ak} |k\rangle \right) \quad N = \frac{1}{\sqrt{\sum_k |V_{ak}|^2}} \]

\[ V_{ag} = \langle a | \hat{H} | g \rangle = N \sum_k V_{ak} \langle a | \hat{H} | k \rangle = N \sum_k |V_{ak}|^2 = \sqrt{\sum_k |V_{ak}|^2} \]

Imaginary part of the self-energy:

\[ \Delta (\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta (\varepsilon - \varepsilon_k) = \pi \frac{1}{N^2} \sum_k |\langle g | k \rangle|^2 \delta (\varepsilon - \varepsilon_k) \]

\[ = \pi \frac{1}{N^2} \rho_g (\varepsilon) = \pi |V_{ag}|^2 \rho_g (\varepsilon) \]
The Green's function slide

Conductance (1,2)

\[ G = \frac{2e^2}{h} \text{Tr} \left[ G_S^R \Gamma_L G_S^A \Gamma_R \right] \]

Central quantity:

\[ G_S^R = \left[ \epsilon^+ S_S - H_S - \Sigma_L^R - \Sigma_R^R \right]^{-1} \]

Self-energies due to leads:

- Left lead: \[ \Sigma_L^R = \left( \epsilon^+ S_{SO} - H_{SO} \right) g_{00}^R \left( \epsilon^+ S_{SO}^+ - H_{SO}^+ \right) \]
- Similar expression for right lead

Shaded area treated within DFT

(1) Meir and Wingreen, PRL 68, 2512 (1992)
(2) Y. Xue et al., Chem. Phys. 281, 151 (2002)
Conductance Formula Applied to Newns-Anderson model

\[
G = \frac{2e^2}{h} \text{Tr} \left[ G_S^R \Gamma_L G_S^A \Gamma_R \right] = \frac{2e^2}{h} \frac{1}{\varepsilon - \varepsilon_a - \Lambda + i \Delta} 2 \Delta_L \frac{1}{\varepsilon - \varepsilon_a - \Lambda - i \Delta} 2 \Delta_R \\
= \frac{2e^2}{h} \frac{4 \Delta_L(\varepsilon) \Delta_R(\varepsilon)}{(\varepsilon - \varepsilon_a - \Lambda(\varepsilon))^2 + \Delta(\varepsilon)^2}
\]

Symmetric Contact: \( \Delta_L(\varepsilon) = \Delta_R(\varepsilon) = \frac{1}{2} \Delta(\varepsilon) \)

\[
G = \frac{2e^2}{h} \frac{\Delta^2}{(\varepsilon - \varepsilon_a - \Lambda)^2 + \Delta^2} = \frac{2e^2}{h} \pi \Delta(\varepsilon) \rho_a(\varepsilon) = \frac{2e^2}{h} \pi^2 |V_{ag}|^2 \rho_g(\varepsilon) \rho_a(\varepsilon)
\]

Wide band -> \( G(\varepsilon) \) Lorentzian shape peaking at \( \varepsilon_a \) with value \( \frac{2e^2}{h} \)
Choice of Basis Set

- For evaluating Kohn-Sham Hamiltonian: \( H_{\text{KS}} = T + V_{\text{eff}} + V_{\text{NL}} \)
- Localized basis set required to separate leads and scattering region
- Systematically converged

Basis set
\[
| i, n \rangle = \phi_i(z) \chi_{i,n}(r_{\perp})
\]

\( i = 0 \)

\( \chi_{i,n}(r_{\perp}) \) solution to 2D Kohn-Sham equation
- Localized at 'site' i
- Using plane waves

\( \phi_i(z) \) localized wavelet at 'site' i
- Compact support
- Non-orthogonal


Wannier Function Basis

- Maximally localized
- Span the set of occupied eigenstates
- Plane wave accuracy
- Minimal basis

Pt wire:

Benzene molecule:

Thygesen, Hansen, Jacobsen, PRL 94, 026405 (2005)

Calzolari, Marzari, Souza, Nardelli, PRB 69, 035108 (2004)
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Partly Occupied Wannier Functions

Make linear combinations of eigenstates (found by plane-wave code) in order to produce localized wave functions.
Unitary transformation to keep orthogonality of states.
Include all occupied states + some more to maximize localization.
--> Bonding-antibonding closing.

Example: Benzene

Thygesen, Hansen, Jacobsen, to be published
Inclusion of Unoccupied States in WF

Maximal localization per WF guides the choice of how many unoccupied states to include.

The relevant unoccupied states are not necessarily lowest in energy.
Partly Occupied Wannier Functions

Pt‐wire

1 σ bond + 5 d‐orbitals

Pt‐wire with Hydrogen molecule

1a) (Pt₆)

2a) (Pt₆‐H₂)

1b)

2b)
Conductance of monatomic wires

Even-odd oscillations in the conductance of monatomic metal wires.

Lang, Avouris, PRL 81, 3515, (1998)

Tsukamoto and Hirose, PRB 66, 161402 (2002)

Lee, Brandbyge et al., PRB 69, 125409 (2004)

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Four-atom Period in Conductance of Aluminum Wires

- 4-atom period in conductance
- \( p \)-orbitals carry current

Three-atom “basis”

Model: Resonance postions obtained from infinite wire
Resonance widths scale as \( 1/N \)

Conductance of Aluminum Wire

The discrete spectrum of an $N$-atom wire follows from the band of the infinite wire:

$$
\epsilon_n^N = \epsilon \left( \frac{n \pi}{E^N} \right), \quad n = 1, 2, \ldots, N
$$

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Four-Atom Period

- The extended nature of the molecular orbitals on the free wire determines the scaling of the resonance width:
  \[ \Delta \propto 1/N \]
- Fermi level is determined by filling factor of the infinite wire:
  \[ f=0.25 \text{ (Al)} , \ f=0.5 \text{ (Na,C,Au)} \]

- For short wires \((N=1,2)\) charge neutrality on the wire is important.
- The oscillations do not decay!
Na versus Al wires

Na less resonant structure

Charge neutrality criterion identical to criterion from infinite wire.
How Do Adsorbates Affect Atomic Chains?

Passivation – closing of conduction channels

$G(\epsilon_F)$ reduced by $1 \, G_0$

$G(\epsilon_F)$ reduced by $2 \, G_0$

H/Pt

Passivation – closing of conduction channels
High Chemical Activity for Low Metal Coordination Numbers

Adsorption Induced Restructuring

- Oxygen adsorption
  - Flexible
  - Stable
  - Conducting
  - May explain long bond lengths in TEM?

- CO adsorption
  - Band gap opens up

H$_2$/Pt Molecular Bridge

- Does H$_2$ dissociate?
- What is the detailed structure?
- Why is H$_2$ conducting?

Molecular Stability in Different Contacts

Usually H₂ dissociates on Pt
  Luntz et al, JCP 93 5240 (1990)
Small barrier for some facets
  Pasteur et al, JCP 106, 8896 (1997)

Bonding of H₂:

\[ E \approx -f \frac{V_a^2}{\varepsilon - C} \]

Bonding at “both ends” essential.

Calculations by Kristian Thygesen
H$_2$/Pt Contacts

Total Energy of PtH$_2$ (PW91)

Dissociated structure suggested by Y. Garcia et al., PRB 69, 041402(R) (2004)
Vibrations

Observation: The observed mode increases its frequency upon stretching!

Problem: The longitudinal center of mass mode is expected to decrease.

Calculated Vibrations

Calculations by Kristian Thygesen
New Measurements

Talk Friday!

Djukic, Thygesen, Untiedt, Smit, Jacobsen, van Ruitenbeek
Conductance of Hydrogen Bridge


\[ d_{\text{H-H}} = 1.0 \, \text{Å} \]
\[ d_{\text{Pt-H}} = 1.76 \, \text{Å} \]
Wannier Function Analysis

1 sigma orbital + 5 d-orbitals per Pt atom
1 s-like orbital for each of the two H atoms

Antibonding state at Fermi level: H₂ bond weakening.
Transport carried by antibonding state!

Bonding state
\[ \epsilon_b = -6.4 \text{ eV} \]

Anti-bonding state
\[ \epsilon_a = 0.1 \text{ eV} \]

Conductance:
\[ G = \frac{2e^2}{h} 2\pi^2 |V_{ag}|^2 \rho_g(\epsilon) \rho_a(\epsilon) \]

Cuevas et al., Nanotechnology 14, R29 (2003)
Garcia et al., PRB 69, 041402 (2004)
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Exact Resonant-Level Model

Parameters from DFT:
\[ \varepsilon_a = 0.1 \text{ eV} \]
\[ V_{ag} = 1.6 \text{ eV} \]
(to one side)

\[ G = \frac{2e^2}{h} 2\pi^2 |V_{ag}|^2 \rho_g(\varepsilon) \rho_a(\varepsilon) \]
Benzene-dithiol/Au

Identifying the simplest “molecular subspace”:
Consider S as part of the leads.

Other calcs:
Emberly, Kirczenow (2001)
Xue and Ratner (2004)

Thygesen, Jacobsen, to be published

But experiments?
Disagreement 2-3 orders of magn.
Lörtscher, Weber, Riel: here
Reed et al. Science (1997)
CO/Pt

Experimental conductance histogram:

Clean Pt: Peak around $1.5 \, G_0$

With CO: Two peaks around $1.2 \, G_0$ and $0.5 \, G_0$

Untiedt, Dekker, Djukic, van Ruitenbeek, PRB 69, 081401, 2004
CO Molecular States

Calculations by Mikkel Strange
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**CO in Pt chains**

Calculated conductance:

3 channels in wire

![Graph showing calculated conductance with electrode spacing (Å) on the x-axis and conductance (G₀) on the y-axis.](image)

- 1.3 $G₀$
- 0.5 $G₀$
CO in Pt chains

- Newns-Anderson Model

  - Two MO determines the conductance
Clean Pt Contact

- **Clean Pt contact - trace**
- **Transmission function**

- Plateau is due to the central atoms “sticking” together
- Conductance for wire $\sim 1.7 \, G_0$

Supercell

- The peak is due to the d-orbitals
CO/Pt

- **Pt contact + CO**

  ![Conductance trace and Energy](image)

  - Binding energy: $\sim -2.5\text{eV}$ -> CO prefers to sit in the contact
  - Discontinuous transition: CO tilts
  - $0.5\ G_0$ plateau caused (at least partly) by asymmetry

  ![Conductance histogram](image)

  Further work required to identify vibrational modes at $1G_0$
Bipyridine conductance: 0.01 $G_0$

Xu and Tao, Science 301, 1221 (2003)
Bipyridine between Gold Contacts

Octanethiol:
Break force: 1.5 ± 0.2 nN
Sometimes very long stretching > 1nm
chain formation?
breaking of Au-Au bonds?
Conductances in agreement with calculations by Tomfohr and Sankey

Bipyridine:
Conductance: 0.01 $G_0$
Break force: 0.8 ± 0.2 nN

Bipyridine Calculation Geometries

Varying coordination number of contacting gold atom.

Stadler, Thygesen, Jacobsen  
Talk by Robert Stadler tomorrow!
Calculations for Bipyridine/Au

Wire

Flat substrate

Break force:
- chain (N=1): 1.6 nN
- adatom (N=3): 1.2 nN
- triangle (N=5): 0.8 nN
- flat surf (N=9): 0.4 nN
- expt: 0.8 +/- 0.2 nN
Bipyridine Bonding

Trend independent of exchange-correlation functional.
HOMO hybridizing with metal states ($V \sim 1.7$ eV)
Bipyridine Conductance

Position of LUMO determined by
1) Coordination number of gold contact atom (local field)
2) Work function (non-local)
Bipyridine Conductance

Experiment: $0.01 \ G_0$
Bipyridine Conductance

Our result:

Calculation by S. Hou et al. (Nanotechnology, 2005) (cluster calculation)
Conductance = 0.0101 $G_0$
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(Nitro-)Benzene in Different Contacts

Gold contact + gold leads

1 polyacetylene + gold leads

2 polyacetylene + gold leads

polyacetylene leads

Robert Stadler, Kristian Thygesen, Karsten W. Jacobsen, to be published
Rotated nitro-group has essentially no effect.
Adding one or two PA units increases the conductance.