Green’s function formalism and its applications to charge and energy transport through nanosystems

Fabian Pauly
“Green function” or “Green's function”?

Other examples: Bessel’s vs. Bessel function

German: “Greensche Funktion”
Charge and heat transport at the smallest scale

Limits of miniaturization of electric circuits?

Heat dissipation & cooling

New architectures

Energy efficiency & powering

„Top-down“ (Material science & physics)

10
1 mm
100
10
1 μm
100
10
1 nm
1 Å

„Bottom-up“ (Chemistry & biology)

Molecular junctions are ideal systems to understand charge & heat transport, heat dissipation, thermoelectricity at the atomic scale
Atomistic modeling of electron and phonon transport

Questions

• What is the electron current through a nanojunction?
• How large is the heat flow?

Challenges to be solved for atomistic modeling

• Material- and molecule-specific description of electronic structure
• Determination of stable contact geometries
• Electric and phononic transport description

Created by STM or mechanically controllable break-junction technique
Outline

Green’s function formalism
• What is a Green’s function?
• Green’s functions in quantum physics
  – Equilibrium Green’s functions
  – Nonequilibrium Green’s functions

Molecular electronics
• Theoretical framework

Electrical properties
• Structure-conductance relationships
• Inelastic effects due to vibrations

Beyond electric conductance
• Thermoelectric properties
• Heat dissipation

Summary & outlook
Some good books


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Summary & outlook
What is a Green’s function?

For a given linear, inhomogeneous differential equation

\[ [z - L(\vec{r})]u(\vec{r}) = f(\vec{r}) \]

define the Green’s function

\[ [z - L(\vec{r})]G(\vec{r}, \vec{r}'; z) = \delta(\vec{r} - \vec{r}') \]

to obtain the solution

\[ u(\vec{r}) = \int G(\vec{r}, \vec{r}'; z) f(\vec{r}') d\vec{r}' \]

If \( u(r) \) describes physically the response of a system to a source \( f(r) \), then \( G(r, r') \) describes the response of the same system to a unit point source located at \( r \).
Green’s function of non-interacting electrons

Time-independent Schrödinger equation

\[ H \psi (\vec{r}) = E \psi (\vec{r}) \]

Define Green’s function via

\[ \left[ E - H \right] G(\vec{r}, \vec{r}', E) = \delta(\vec{r} - \vec{r}') \]

Definition of retarded and advanced Green’s function in energy space

\[ G^{r,a}(E) = (E \pm i\eta - H)^{-1} \]

In a particular one-electron basis the different Green functions will be

\[ G^{r,a}_{ij}(E) = \left< i \left| G^{r,a}(E) \right| j \right> \]
Spectral representation and Dyson equation

Spectral representation

\[ G^{r,a}(E) = \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{E \pm i\eta - \varepsilon_n} \]

non-interacting electrons

interacting electrons

\[ G^{r,a}(E) = \sum_m \frac{\langle\psi^N_0 | c_{i\sigma} | \psi^N_m\rangle \langle\psi^N_m | c_{j\sigma}^\dagger | \psi^N_0\rangle}{E - (E^{N+1}_m - E^N_0) \pm i\eta} + \sum_m \frac{\langle\psi^N_0 | c_{j\sigma}^\dagger | \psi^{N-1}_m\rangle \langle\psi^{N-1}_m | c_{i\sigma} | \psi^N_0\rangle}{E - (E^{N-1}_m - E^N_0) \pm i\eta} \]

Dyson equation

\[ H = H_0 + V \quad \text{Hamiltonian with perturbation} \]

\[ G(E) = (E - H_0 - V)^{-1} = \left[ G^{-1}_0(E) - V \right]^{-1} = G_0(E) \sum_{n=0}^{\infty} VG_0(E) \]

\[ G(E) = G_0(E) + G_0(E)VG(E) = G_0(E) + G(E)VG_0(E) = G_0(E) + \sum_{n=0}^{\infty} \frac{VG_0(E)}{1 + \frac{VG_0(E)}{1 + \frac{VG_0(E)}{1 + \frac{VG_0(E)}{1 + \cdots}}}} \]

\[ G(E) = G_0(E) + G_0(E)\Sigma(E)G(E) \]
Nonequilibrium Green’s functions – Keldysh formalism

\[ H = H_0 + V(t) \]  
\[ \text{Perturbation with explicit time dependence} \]

Noninteracting electrons in equilibrium

\[ \langle A(t) \rangle = \frac{\langle \phi_0 \mid S(-\infty, t) A_I(t) S(t, -\infty) \mid \phi_0 \rangle}{\langle \phi_0 \mid S(-\infty, t) S(t, -\infty) \mid \phi_0 \rangle} \]

\[ S(t, t_0) = T \exp \left[ -i \int_{t_0}^{t} dt V_I(t) \right] \]

\[ S_c(\infty, -\infty) = S_-(\infty, 0) S_+(-\infty, -\infty) \]

\[ T \text{ and } T_c: \text{ time ordering operators along real axis and contour} \]

Keldysh contour

\[ -\infty \quad \text{upper branch (+)} \quad +\infty \]

\[ -\infty \quad \text{lower branch (-)} \]
Nonequilibrium Green’s functions – Keldysh formalism

\[ G_{ij}(t_\alpha, t_\beta') = -i \langle \Psi_H | T_c \left[ c_i(t_\alpha)c_j^\dagger(t_\beta') \right] | \Psi_H \rangle = G_{ij}^{\alpha,\beta}(t, t'), \quad \alpha, \beta = +, - \]

\( G(t, t') = \begin{pmatrix} G^{++}(t, t') & G^{+-}(t, t') \\ G^{-+}(t, t') & G^{--}(t, t') \end{pmatrix} \)

\[ G^r = G^{++} - G^{--} = -G^{--} + G^{++} \]

\[ G^a = G^{++} - G^{--} = -G^{--} + G^{++} \]

\[ G^K = G^{++} + G^{--} = G^{++} + G^{--} \]

\[ G^{r,a} = g^{r,a} + g^{r,a}\Sigma^{r,a} G^{r,a} \]

\[ G^{+-} = (1 + G^r\Sigma^r)g^{+-} (1 + \Sigma^a G^a) - G^r\Sigma^{+-} G^a \]

\[ G^{-+} = (1 + G^r\Sigma^r)g^{-+} (1 + \Sigma^a G^a) - G^r\Sigma^{-+} G^a \]

Current through a nanojunction

Expression for the current readily expressed through Keldysh Green’s functions

\[
I = \frac{ie}{\hbar} \sum_{i \in L, j \in C, \alpha, \beta} \left( H_{i\alpha, j\beta} \langle c_{i\alpha, \sigma}^\dagger c_{j\beta, \sigma} \rangle - H_{j\beta, i\alpha} \langle c_{j\beta, \sigma}^\dagger c_{i\alpha, \sigma} \rangle \right)
\]

\[
I = \frac{2e}{\hbar} \int_{-\infty}^{\infty} dE \text{Tr} \left[ G_{CL}^+(E) H_{LC} - H_{CL} G_{LC}^-(E) \right]
\]

\[
I = \frac{2e}{\hbar} \int_{-\infty}^{\infty} dE \tau(E, V) (f_L - f_R)
\]

Landauer formula for the current

Transport elastic and coherent; all quantum interference paths
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Summary & outlook
Atomistic modeling of charge transport through nanosystems

Challenges

- Material- and molecule-specific *ab-initio* description of electronic structure
  → Density functional theory (DFT)
- Determination of stable contact geometries, vibrations, electron-phonon couplings
  → DFT
- Electric transport
  → Green’s function description

TURBOMOLE software

- Quantum chemistry software package
- DFT module
- Localized Gaussian atomic orbitals
  → Very accurate and efficient

Member of development team
Landauer scattering theory for electron transport

Transport as scattering problem

\[ I \xrightarrow{S} t(E) \xrightarrow{r(E)} \]

Theoretical model of contact

\[ \tau(E) + R(E) = |t(E)|^2 + |r(E)|^2 = 1 \]

Landauer formula for conductance

\[ G = \frac{2e^2}{h} \tau(E_F) \]  
Quantum of conductance

\[ G_0 = \frac{2e^2}{h} \approx 77 \ \mu S = (13 \ k\Omega)^{-1} \]

Assumptions: Elastic, phase coherent electron transport  
\[ \rightarrow \] Scattering region shorter than inelastic scattering lengths

Electron reservoirs

Scattering region

Spin degeneracy
Electronic structure

Schrödinger equation in Born-Oppenheimer approximation:

\[ H_{el} \psi = E \psi \]

\[
H_{el} = -\frac{\hbar^2}{2m_e} \sum_{\mu=1}^{N} \nabla_{\mu}^2 - \sum_{\mu=1}^{N} \sum_{A=1}^{M} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{\mu A}} + \sum_{\mu=1}^{N} \sum_{\nu>\mu}^{M} \frac{e^2}{4\pi\varepsilon_0 r_{\mu \nu}} = T + V_{Ne} + V_{ee}
\]

DFT: Kohn-Sham ansatz


\[ E[\rho] = T_s[\rho] + J[\rho] + E_{Ne}[\rho] + E_{XC}[\rho] \]

• Self-consistent, effective single-particle theory
• Kohn-Sham eigenvalues interpreted as quasiparticle energies

Other methods: DFT+Σ, GW, LDA+DMFT
### Landauer scattering theory and Green's functions

**Conductance**
\[ G = G_0 \tau(E_F) \]

**Transmission**
\[ \tau(E) = \text{Tr} \left[ \Gamma_L(E) G_{CC}^r(E) \Gamma_R(E) G_{CC}^a(E) \right] \]

**Conductance quantum**
\[ G_0 = 2e^2/h \]

**Green's function**
\[ G_{CC}^r = \left( ES_{CC} - H_{CC} - \Sigma_L^r - \Sigma_R^r \right)^{-1} \]

**Self energies** \((X=L,R)\)
\[ \Sigma_X^r = \left( H_{CX} - ES_{CX} \right) g_{XX}^r (H_{XC} - ES_{XC}) \]

**Linewidth broadening matrix** \(\Gamma_X = -2 \text{Im} \left[ \Sigma_X^r \right] \)

**Cluster-based ansatz**


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**„DFT+NEGF“**

NEGF: Nonequilibrium Green's functions

see also
Level alignment at metal-molecule contact

Physical effects influencing level alignment
- Interfacial charge rearrangement
- Quantum mechanical coupling
- Nonlocal surface polarization

Spectral adjustment: “DFT+Σ“

GW quasiparticle methods
Overview of electronic structure methods

Quasiparticle equation
\[ \hat{h}_0(r)\psi_i(r) + \int \Sigma(r,r';\varepsilon_i/\hbar)\psi_i(r')d^3r' = \varepsilon_i\psi_i(r) \]

Approximations to the self-energy

<table>
<thead>
<tr>
<th>Method</th>
<th>Self-energy expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hartree-Fock</td>
<td>[ \Sigma^{HF}(r,r') = i\hbar G(r,r';-\eta)v(r,r') ]</td>
</tr>
<tr>
<td>DFT</td>
<td>[ \Sigma^{DFT}(r,r') = V_{XC}(r)\delta(r-r') ]</td>
</tr>
<tr>
<td>GW</td>
<td>[ \Sigma^{GW}(r,r';\omega) = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} G(r,r';\omega+\omega')W(r,r';\omega')d\omega' ]</td>
</tr>
</tbody>
</table>

Coulomb interaction \[ v(r,r') = e^2 / (4\pi \varepsilon_0 |r-r'|) \]

Screened Coulomb interaction \[ W(r,r';\omega) = \int \varepsilon^{-1}(r,r'';\omega)v(r'',r')d^3r'' \]

Dielectric function \[ \varepsilon(r,r';\omega) = \delta(r,r') - \int v(r,r'')P(r'',r';\omega)d^3r'' \]

Polarization function \[ P(r,r';\tau) = -i\hbar G(r,r';\tau)G(r',r;\tau) \]

“HF” in screened Coulomb interaction
The „band gap“ problem

C. Friedrich and A. Schindlmayr, NIC Series, Vol. 31, pp. 335-355, 2006
Phonon dispersion relations

Figure 2.9. Phonon dispersion curves calculated for the semiconductor GaAs [154]. The points are from experiment and the curves from density functional theory using the response function method (Ch. 19). Similar agreement is found for the entire family of semiconductors. Calculations for many types of materials, e.g. in Figs. 19.4 and 19.5, have shown the wide applicability of this approach.


Spring constants needed $K_{i\mu,j\nu} = \frac{\partial^2 E}{\partial R_{i\mu} \partial R_{j\nu}}$
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Summary & outlook
Structure-conductance relationships

What is the influence of conjugation on molecular conductance?

Transition amplitude between rings $\propto \cos \phi$

Transmission or conductance: $G \propto \cos^2 \phi$
Influence of conjugation on conductance

A. Mishchenko et al., Nano Lett. 10, 156 (2010)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Structure</th>
<th>Torsion angle $\phi$ (X-Ray, Acetyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
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<td>36.4°</td>
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<tr>
<td>M2</td>
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<td>1.1°</td>
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<tr>
<td>M3</td>
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<td>16.8°</td>
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<td>M5</td>
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<td>71.5°</td>
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<tr>
<td>M8</td>
<td><img src="image8.png" alt="Image" /></td>
<td>89.0°</td>
</tr>
</tbody>
</table>

Tailor-made side groups gradually change the torsion angle

See also:
Influence of conjugation on conductance

A. Mishchenko et al., Nano Lett. 10, 156 (2010)

Experiment

\[
\frac{G}{G_0} \times 10^3
\]

\[\cos^2 \varphi\]

Transmission dominated by molecular π system (independent of binding site to Au)

Hollow-Hollow


→ DFT allows to identify charge transport mechanism

→ Change by more than 1 order of magnitude
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Summary & outlook
Inelastic interactions due to vibrations

Is there a molecule in the contact? → Vibrations yield a fingerprint

Inelastic electron tunneling spectra (IETS)
- Energy of vibrational mode: $\hbar \omega$
- Conductance changes, if the voltage is $eV \approx \hbar \omega$.
- Second derivative of the current shows changes clearly

Goal:
Determine inelastic electron tunneling spectra from first principles (DFT)

See for instance:
J. C. Cuevas and E. Scheer, Molecular Electronics, World Scientific (2010)
Inelastic transport method

\[ H = H_e + H_{vib} + H_{e-vib}; \]
\[ H_e = \sum_{i,j} d_i^\dagger H_{ij} d_j; \]
\[ H_{vib} = \sum_\alpha \hbar \omega_\alpha b_\alpha^\dagger b_\alpha; \]
\[ H_{e-vib} = \sum_{i,j} \sum_\alpha d_i^\dagger \lambda^\alpha_{ij} d_j (b_\alpha^\dagger + b_\alpha) \]

\[ \lambda^\alpha_{ij} = \sqrt{\frac{\hbar}{2\omega_\alpha}} \sum_{k,\mu} \langle i | \nabla_{k,\mu} H_e \big| \psi_0 \rangle j \rangle A_{k,\mu,\alpha} \]

→ Implementation in TURBOMOLE using density functional perturbation theory (DFPT) & “semianalytical” derivatives (available in official TURBOMOLE version)

Lowest-order expansion of current in electron-vibration coupling

\[ I = I_{el} + \delta I_{el} + I_{inel} \]

\[ I_{el} = \frac{2e}{\hbar} \int dE \text{Tr}[G^r \Gamma_R G^a \Gamma_L](f_L - f_R) \]

\[ \delta I_{el} = \frac{4e}{\hbar} \int dE \text{Re} \text{Tr}[(\Gamma_L G^r \Sigma^r_{e-vib} G^r \Gamma_R G^a)](f_L - f_R) \]

\[ I_{inel} = -i \frac{2e}{\hbar} \int dE \text{Tr}\left[ G^a \Gamma_L G^r \left\{ (f_L - 1) \Sigma^<_{e-vib} - f_L \Sigma^>_{e-vib} \right\} \right] \]

Molecules on surfaces

Problem: Molecules normally lie flat on a metal surface
→ Decoupling of functional molecular unit from surface needed to avoid quenching

Tailor-made tripodal platform delivers 3D structure

Is the molecule positioned on the surface as intended, and how does the current proceed?

M. A. Karimi et al., Nanoscale 8, 10582 (2016)
Current path for a conductive molecular wire on a tripodal platform

- Elastic transmission agrees with average experimental conductance, $G \approx 10^{-3} G_0$
  → indicates right junction geometry
- Inelastic tunneling spectra confirm transport through backbone

Theory: DFT+$\Sigma$

M. A. Karimi et al., Nanoscale 8, 10582 (2016)
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Summary & outlook
Understanding thermoelectrics at the atomic scale

Thermoelectric elements
- Conversion of waste heat into electrical energy
- Nanorefrigerators

Figure of merit characterizes thermoelectric power generation efficiency: \( ZT = S^2 G T / \kappa \)

Thermopower \( S \)
Electric conductance \( G \)
Temperature \( T \)
Thermal conductance \( \kappa \)

\[ \kappa = \kappa_{el} + \kappa_{ph} \]

Enhancement of \( ZT \) through appropriate nanostructuring

How large is \( ZT \) for molecular junctions?
How do \( \kappa_{el} \) and \( \kappa_{ph} \) compare?
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  – Phonon thermal transport
  – Figure of merit
• Heat dissipation

Summary & outlook
Why thermopower?

Seebeck effect

Landauer-Büttiker formalism

Thermopower (electronic contribution):

\[ S = -\frac{\Delta V}{\Delta T} \approx -\frac{\pi^2 k_B^2}{3e} k_B T \frac{\partial \ln(\tau(E))}{\partial E} \]

- Sign of \( S \) distinguishes “electron type“ and „hole type“ conduction

→ Hint to position of \( E_F \) with respect to HOMO and LUMO

Theory suggestion

First experiment
Theoretical studies of the thermopower

**Length dependence**

\[ \tau(E) \approx \alpha(E) \exp(-\beta(E)N) \]

\[ S = S^{(0)} + S^{(1)}N \]

Exponential decay of conductance with length (tunneling) leads to linear increase of thermopower


**Influence of conjugation**

Change of conjugation leads only to slight variation of thermopower


**Metallic atomic contacts**


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Summary & outlook
Phonon thermal transport

Phonon density of states of bulk gold
- Extracted from finite clusters
- Good agreement with experiment

![Graph showing phonon density of states](image)

### Force constant matrix

\[
K_{ij} = \frac{1}{\sqrt{M_i M_j}} \frac{\partial^2 E}{\partial R_i \partial R_j}
\]

### Phonon transmission

\[
\tau_{ph}(E) = \text{Tr} \left[ \Lambda_L(E) D^r(E) \Lambda_R(E) D^a(E) \right]
\]

### Linear response properties

**Phonons:**

\[
\kappa_{ph} = \frac{1}{\hbar} \int_0^\infty dE \tau_{ph}(E) \frac{\partial n}{\partial T} E
\]

**Electrons:**

\[
G = G_0 K_0 \quad S = -\frac{K_1}{eTK_0}
\]

\[
\kappa_{el} = \frac{2}{\hbar T} \left( K_2 - \frac{K_1^2}{K_0} \right)
\]

\[
K_n = \int dE \tau_{el}(E) \left( -\frac{\partial f}{\partial E} \right) (E - \mu)^n
\]

Heat transport at the nanoscale

Growing interest in heat transport at the nanoscale

**Goal:** Transfer knowledge on nanoelectronics to nanophononics

**State of the art – Experiments**
- Experiments with SAMs show chemical sensitivity (length, anchoring groups, ...)

IBM Zurich:

→ Single-molecule sensitivity is a goal of several experimental groups
Length dependence of the thermal conductance

Alkane single-molecule junctions
- Chains with 2 to 30 units
- Units CY₂ with Y=H or F
- Anchor group X=S or NH₂

→ Thermal conductance rather length-independent for 5 or more CY₂ units

J. C. Klöckner et al., arXiv:1609.03827
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Summary & outlook
Figure of merit without phonon thermal transport

\[ \kappa_{el} = \frac{S^2 GT}{\kappa_{el}} \]

Theory: DFT+\( \Sigma \)
Figure of merit including phonon thermal transport

- $\kappa_{ph}$ cannot be ignored for realistic estimate of $ZT$

$$Z_{el}T = \frac{S^2 GT}{\kappa_{el}}$$

$\kappa_{ph}$ cannot be ignored for realistic estimate of $ZT$

Outlook: Higher $ZT$ junctions, role of anharmonicities, …

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Summary & outlook
Heat dissipation in atomic-scale junctions

Dimensions of the contact region in atomic-scale junctions are much smaller than the inelastic scattering length.

→ Transport is elastic and heat dissipation takes place inside the electrodes.

Is the heat dissipated equally in both electrodes? What is the relation between the dissipated heat and electronic structure?

W. Lee et al., Nature 498, 209 (2013)
Probing heat dissipation

\[ R_{J,P,S}: \text{Thermal resistance of junction, probe, substrate} \]

\[ R_J \gg R_P, R_S \]

\[ \Delta V_{TC} = -S_{TC} \times \Delta T_{TC} \]

Thermovoltage \quad Thermopower \quad Temperature rise

\[ T_P = T_{Amb} + \Delta T_{TC} \]

\[ Q_P(V) = \frac{\Delta T_{TC}}{R_P} \]

Power dissipation

\[ Q_P(V) + Q_S(V) = Q_{Total}(V) = I \times V \]

W. Lee et al., Nature 498, 209 (2013)
Benzenediisonitrile (BDNC) single-molecule junctions

A positive (negative) bias corresponds to a scenario, where the probe is grounded, while the substrate is at a higher (lower) potential.

- Heat dissipation in the electrodes of Au-BDNC-Au junctions is bias-polarity-dependent and thus unequal.
- Why is the heat dissipation in the electrodes unequal in spite of the symmetric geometry of the molecular junctions?
Landauer theory of heat dissipation

Power dissipated in the electrodes

\[ Q_P(V) = \frac{2}{h} \int_{-\infty}^{\infty} (\mu_P - E) \tau(E, V) [f_P(E, \mu_P) - f_S(E, \mu_S)] dE \]

\[ Q_S(V) = \frac{2}{h} \int_{-\infty}^{\infty} (E - \mu_S) \tau(E, V) [f_P(E, \mu_P) - f_S(E, \mu_S)] dE \]

Energy conservation: \( Q_P(V) + Q_S(V) = IV = Q_{Total}(V) \)

When the heat equally dissipated in both electrodes? \( Q_P(V) = Q_S(V), \) if \( \tau(E, V) = \tau(-E, V) \)

Electron-hole symmetry implies equal dissipation

When is the power dissipation independent of bias polarity? \( Q_P(V) = Q_P(-V), \) if \( \tau(E, V) = \tau(-E, -V) \)
Landauer theory of heat dissipation

Conclusion from theoretical considerations

The heat dissipation in the electrodes of atomic-scale contacts is, in general, asymmetric and depends on both the bias polarity and the nature of the majority carriers (electrons vs. holes).

Low-bias expansions

\[ Q_P(V) - Q_P(-V) = 2TGSV + O(V^2) \]

Temperature \( T \)
Conductance \( G \)
Thermopower \( S \)

Prediction

Heating asymmetry should change sign, if sign of \( S \) is changed.

W. Lee et al., Nature 498, 209 (2013)
Asymmetric heat dissipation: simple picture

- An electron flows elastically through the contact with energy $E$, leaving a hole behind.
- The electron thermalizes and dissipates an energy ($E-\mu_S$) in the substrate.
- The hole left in the probe is filled by an electron releasing an energy ($\mu_P - E$) in the probe.
- For hole conduction, the heating in the probe is stronger than in the substrate.
- The opposite is true for electron conduction.

→ An energy-dependent transmission leads to asymmetric heating.
Benzenediisonitrile (BDNC) single-molecule junctions: Comparison between theory & experiment

CN-anchors lead to electron conduction
→ Power dissipation higher for negative bias

W. Lee et al., Nature 498, 209 (2013)
Benzenediamine (BDA) single-molecule junctions: Comparison between theory and experiment

NH$_2$-anchors lead to hole conduction
→ Power dissipation higher for positive bias

W. Lee et al., Nature 498, 209 (2013)
Green’s function formalism
• What is a Green’s function?
• Green’s functions in quantum physics
  – Equilibrium Green’s functions
  – Nonequilibrium Green’s functions

Molecular electronics
• Theoretical framework

Electrical properties
• Structure-conductance relationships
• Inelastic effects due to vibrations

Beyond electric conductance
• Thermoelectric properties
• Heat dissipation

Summary & outlook
Summary – Electron and phonon transport

Electrical current

\[ I = \frac{1}{h} \int dE 2e\tau(E) \left[ f_L(E) - f_R(E) \right] \]

Heat current from electrons

\[ I^\text{el}_Q = \frac{1}{h} \int dE 2(E - \mu)\tau(E) \left[ f_L(E) - f_R(E) \right] \]

Heat current from phonons

\[ I^\text{ph}_Q = \frac{1}{h} \int dE E\tau_{\text{ph}}(E) \left[ n_L(E) - n_R(E) \right] \]

Electrical conductance

\[ G = \frac{2e^2}{h} \int dE \tau(E) \left( -\frac{\partial f}{\partial E} \right) \]

Thermal conductance

\[ \kappa_{\text{ph}} = \frac{\pi^2 k_B^2 T}{3h} \int dE \tau_{\text{ph}}(E) \left[ 3 \left( \frac{E}{k_B T} \right)^2 \left( -\frac{\partial n}{\partial E} \right) \right] \]
Particle current (fermionic $^6$Li atoms)

$$I = \frac{1}{h} \int dE \tau(E) \left[ f_L(E) - f_R(E) \right]$$
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Summary

Structure-conductance relationship
Conjugation has strong impact on molecular conductance

Inelastic electron tunneling spectra
reveal orientation of tripodal platform on metal surface

Thermopower of single-molecule junctions and atomic contacts
can be understood based on electronic structure

Phonon thermal conductance of single-molecule junctions
for alkanes rather length-independent and ballistic

Figure of merit of molecular contacts
needs phonon thermal contribution for realistic estimate

Heat dissipation in atomic-scale junctions
connected to electronic structure and thermoelectric properties

Outlook
Electronic structure method development (DFT & quasiparticle methods in TURBOMOLE),
e-ph and e-e interactions, spin-dependent electron transport, phonon transport
(anharmonic effects), nanoscale thermoelectrics, …