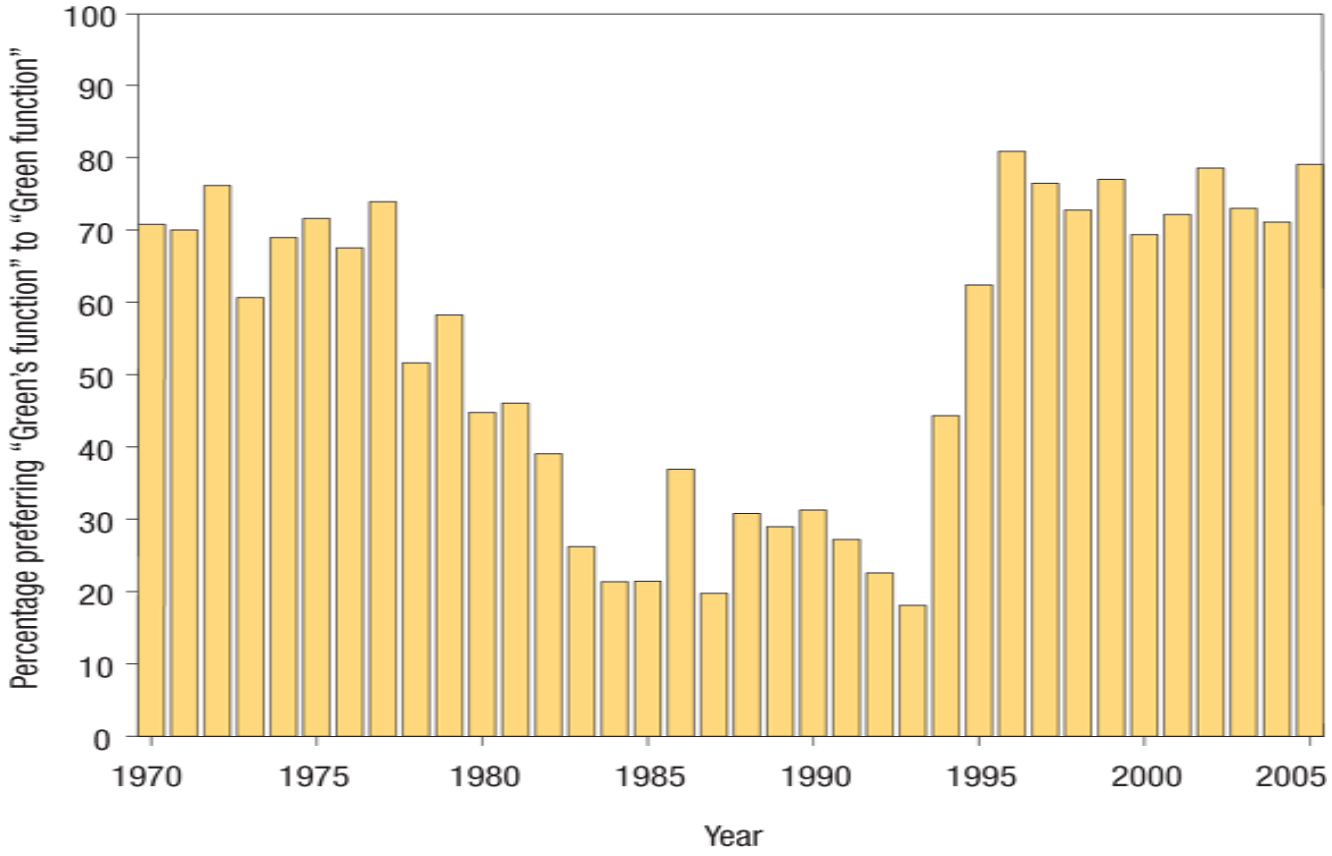
Universität Konstanz

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

Fabian Pauly

Bad Honnef, 20.09.2016

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



M. C. M. Wright, Nature Physics 2, 646 (2006)

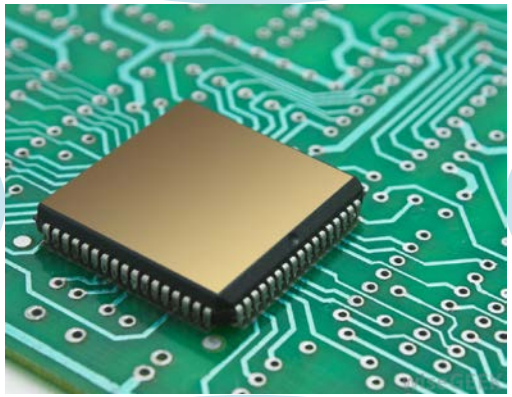
Other examples: Bessel‘s vs. Bessel function

German: “Greensche Funktion”

Charge and heat transport at the smallest scale

Limits of miniaturization of electric circuits?

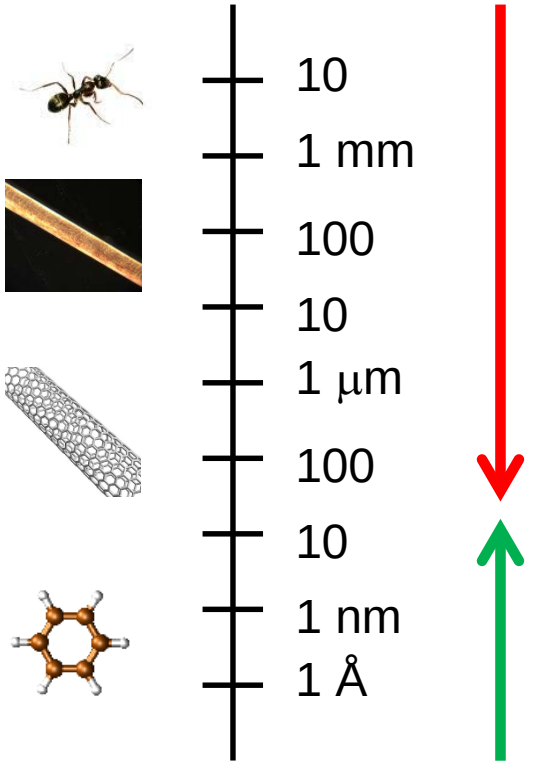
Heat dissipation & cooling



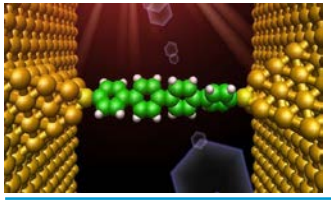
New architectures

Energy efficiency & powering

„Top-down“ (Material science & physics)

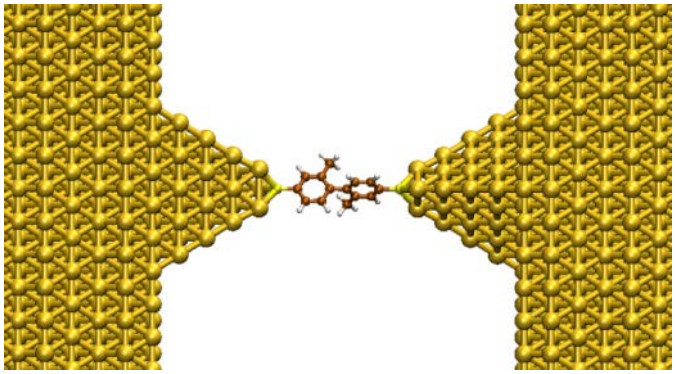


„Bottom-up“ (Chemistry & biology)



Molecular junctions are ideal systems to understand charge & heat transport, heat dissipation, thermoelectricity at the atomic scale

Atomistic modeling of electron and phonon transport



Created by STM or mechanically controllable break-junction technique

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

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

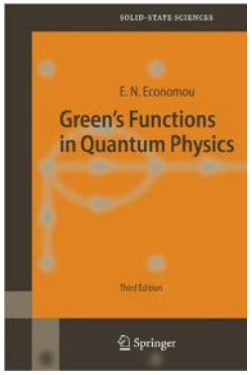
- Structure-conductance relationships
- Inelastic effects due to vibrations

Beyond electric conductance

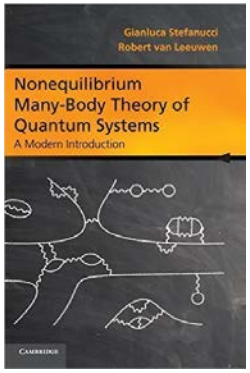
- Thermoelectric properties
- Heat dissipation

Summary & outlook

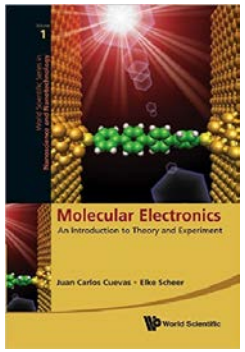
Some good books



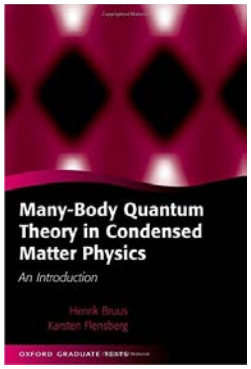
Green's Functions in Quantum Physics,
E. N. Economou,
Springer (2006)



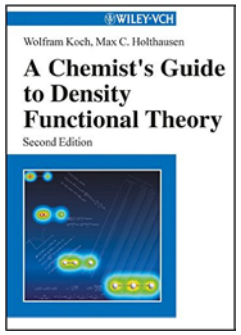
Nonequilibrium Many-Body Theory of Quantum Systems: A Modern Introduction,
G. Stefanucci and R. van Leeuwen,
Cambridge University Press (2013)



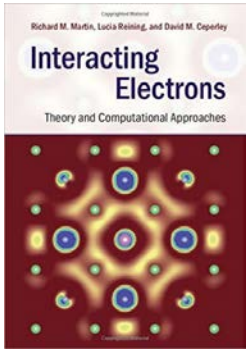
Molecular Electronics: An Introduction to Theory and Experiment,
J. C. Cuevas and E. Scheer,
World Scientific Publishing Company (2010)



Many-Body Quantum Theory in Condensed Matter Physics: An Introduction,
H. Bruus and K. Flensberg,
Oxford University Press (2004)



A Chemist's Guide to Density Functional Theory,
W. Koch and Max C. Holthausen,
John Wiley & Sons (2001)



Interacting Electrons: Theory and Computational Approaches,
R. M. Martin, L. Reining, D. M. Ceperley,
Cambridge University Press (2016)

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

What is a Green‘s function?

For a given linear, inhomogeneous differential equation

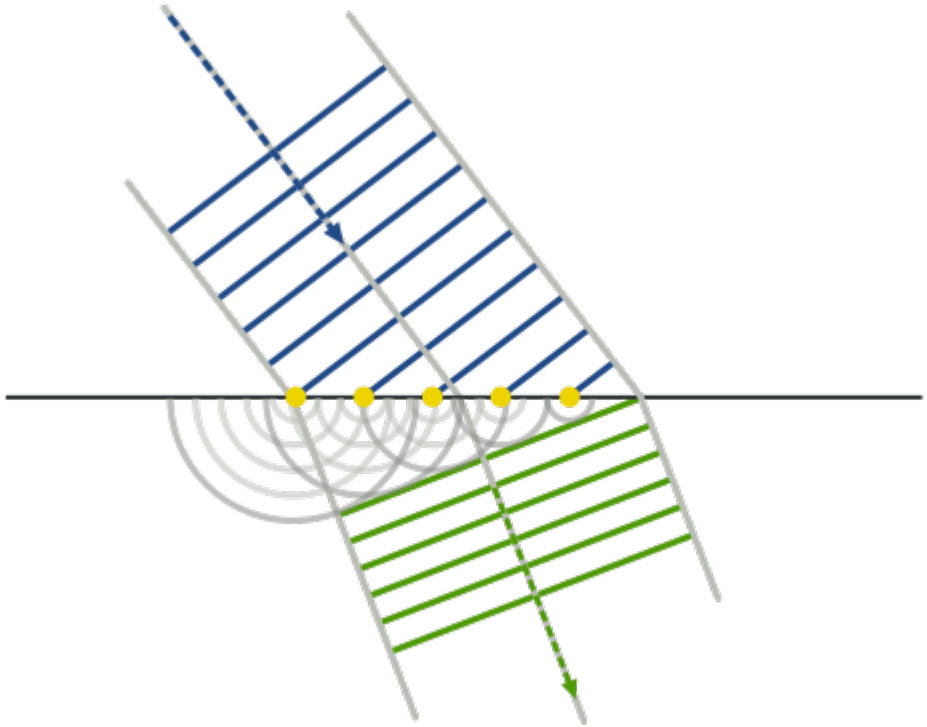
$$\left[z - L(\vec{r})\right] u(\vec{r}) = f(\vec{r})$$

define the Green‘s function

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

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

$$G^{r,a}_{ij}(E) = \left\langle i \middle| G^{r,a}(E) \middle| j \right\rangle$$

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

$$\longrightarrow \quad G_{ij}^{r,a}(E)=\sum_m \frac{\langle\psi_0^N|c_{i\sigma}|\psi_m^{N+1}\rangle\langle\psi_m^{N+1}|c_{j\sigma}^\dagger|\psi_0^N\rangle}{E-\left(E_m^{N+1}-E_0^N\right)\pm i\eta}+\sum_m \frac{\langle\psi_0^N|c_{j\sigma}^\dagger|\psi_m^{N-1}\rangle\langle\psi_m^{N-1}|c_{i\sigma}|\psi_0^N\rangle}{E-\left(E_m^{N-1}-E_0^N\right)\pm i\eta}$$

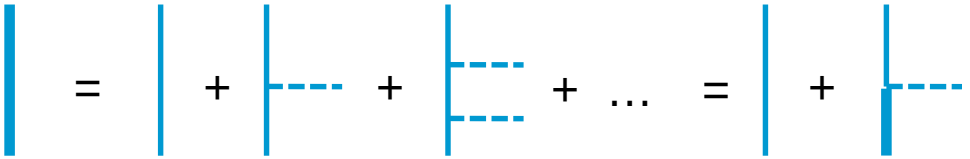
Dyson equation

$H=H_0+V$ Hamiltonian with perturbation

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

$$G(E)=G_0(E)+G_0(E)VG(E)$$

$$G(E)=G_0(E)+G(E)VG_0(E)$$



$$\longrightarrow \quad G(E)=G_0(E)+G_0(E)\Sigma(E)G(E)$$

Nonequilibrium Green's functions – Keldysh formalism

$H = H_0 + V(t)$ ← Perturbation with explicit time dependence

↑ Noninteracting electrons in equilibrium

$$\langle A(t)\rangle = \frac{\langle \phi_0 | S(-\infty,t) A_I(t) S(t,-\infty) | \phi_0 \rangle}{\langle \phi_0 | S(-\infty,t) S(t,-\infty) | \phi_0 \rangle}$$

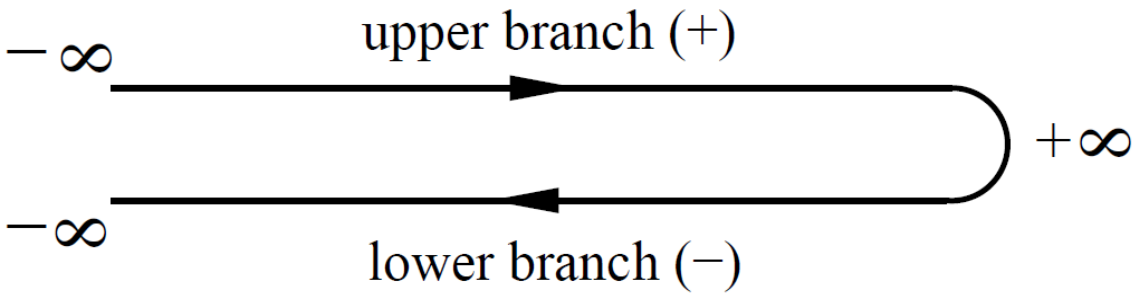
$$S(t,t_0) = T \exp\left[-i \int_{t_0}^{t} dt V_I(t) \right]$$

$$\langle A(t)\rangle = \frac{\langle \phi_0 | T_c \left[A_I(t) S_c(\infty,-\infty) \right] | \phi_0 \rangle}{\langle \phi_0 | S_c(\infty,-\infty) | \phi_0 \rangle}$$

$$S_c(\infty,-\infty) = S_-(-\infty,\infty) S_+(\infty,-\infty)$$

T and T_c: time ordering operators along real axis and contour

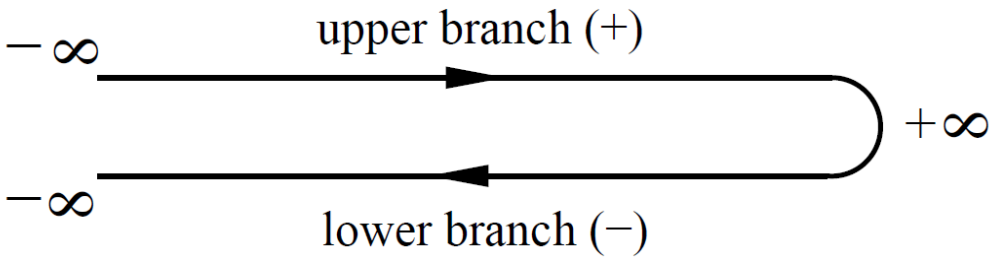
Keldysh contour



Nonequilibrium Green‘s functions – Keldysh formalism

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

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



$$G^r = G^{++} - G^{-+} = -G^{--} + G^{-+}$$
$$G^a = G^{++} - G^{-+} = -G^{--} + G^{-+}$$
$$G^K = G^{++} + G^{--} = G^{+-} + G^{-+}$$

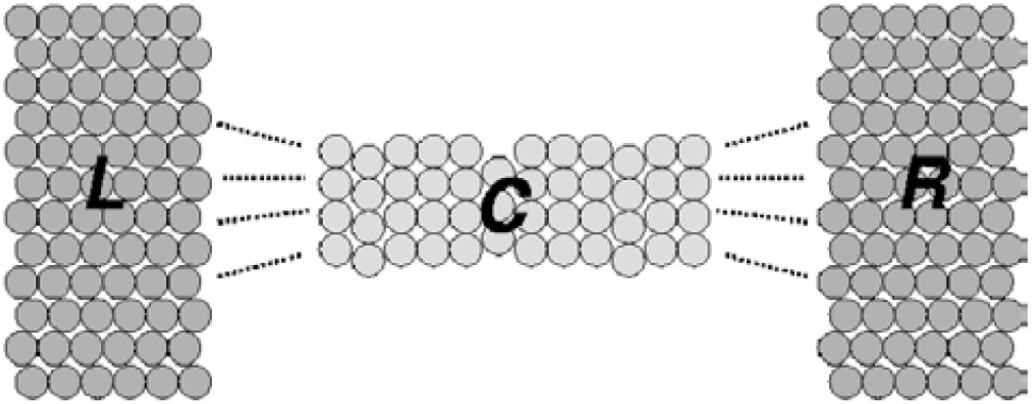
triangular representation

$$\begin{pmatrix} 0 & G^a \\ G^r & G^K \end{pmatrix}$$

$$G^{r,a} = g^{r,a} + g^{r,a}\Sigma^{r,a}G^{r,a}$$
$$G^{+-} = (1+G^r\Sigma^r)g^{+-}(1+\Sigma^a G^a) - G^r\Sigma^{+-}G^a$$
$$G^{-+} = (1+G^r\Sigma^r)g^{-+}(1+\Sigma^a G^a) - G^r\Sigma^{-+}G^a$$

J. C. Cuevas and E. Scheer, World Scientific Publishing Company (2010)

Current through a nanojunction



$$H = \sum_{ij,\alpha\beta,\sigma} H_{i\alpha,j\beta} c^{\dagger}_{i\alpha,\sigma} c_{j\beta,\sigma}$$

$$H = \begin{pmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{CR} \\ 0 & H_{RC} & H_{RR} \end{pmatrix}$$

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

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

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \,\mathrm{Tr}\left[G^{+-}_{CL}(E) H_{LC} - H_{CL} G^{+-}_{LC}(E) \right]$$

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \,\tau(E,V)\left(f_L - f_R \right)$$ ← Landauer formula for the current

Transport elastic and coherent; all quantum interference paths

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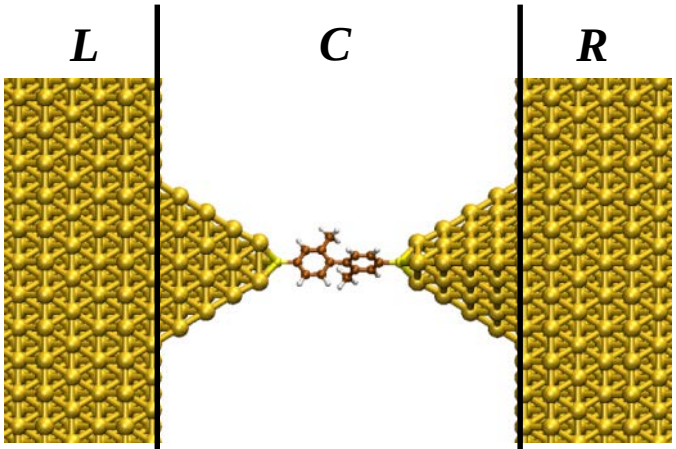
Summary & outlook

Atomistic modeling of charge transport through nanosystems



Electron reservoir | Scattering region | Electron reservoir

TURBOMOLE software
- Quantum chemistry software package
- DFT module
- Localized Gaussian atomic orbitals

→ Very accurate and efficient

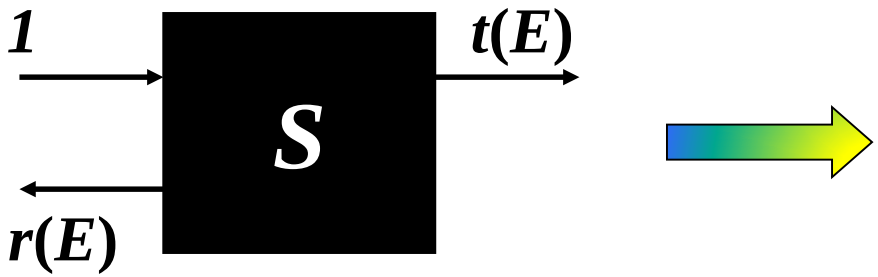
Member of development team

Challenges

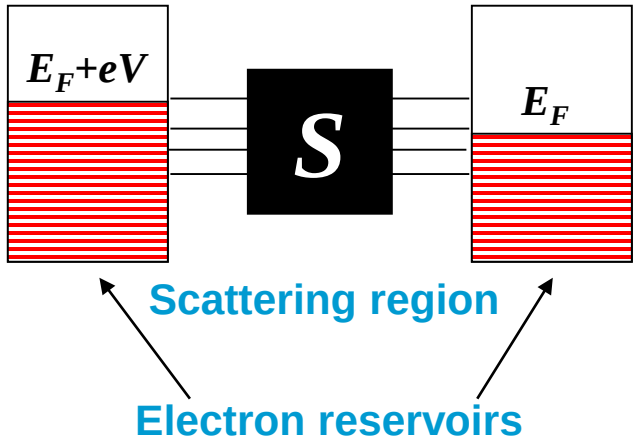
- Material- and molecule-specific a*b-initio* description of electronic structure
  → Density functional theory (DFT)
- Determination of stable contact geometries, vibrations, electron-phonon couplings
  → DFT
- Electric transport
  → Green's function description

Landauer scattering theory for electron transport

Transport as scattering problem



Theoretical model of contact



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

Landauer formula for conductance

Spin degeneracy

$$G = \frac{2e^2}{h}\tau(E_F)$$

Quantum of conductance

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

Assumptions: Elastic, phase coherent electron transport
→ Scattering region shorter than inelastic scattering lengths

Electronic structure

Schrödinger equation in Born-Oppenheimer approximation:

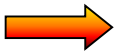
$$H_{el}\psi = E\psi$$

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

DFT: Kohn-Sham ansatz

W. Kohn et al., Phys. Rev. 140, A1133 (1965)

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



- 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

$$\tau(E) = \mathrm{Tr}\left[\Gamma_L(\mathrm{E}) G^r_{CC}(E) \Gamma_R(E) G^a_{CC}(E)\right]$$

Conductance quantum $G_0 = 2e^2/h$

Green‘s function

$$G^r_{CC} = \left(ES_{CC} - H_{CC} - \Sigma^r_L - \Sigma^r_R\right)^{-1}$$

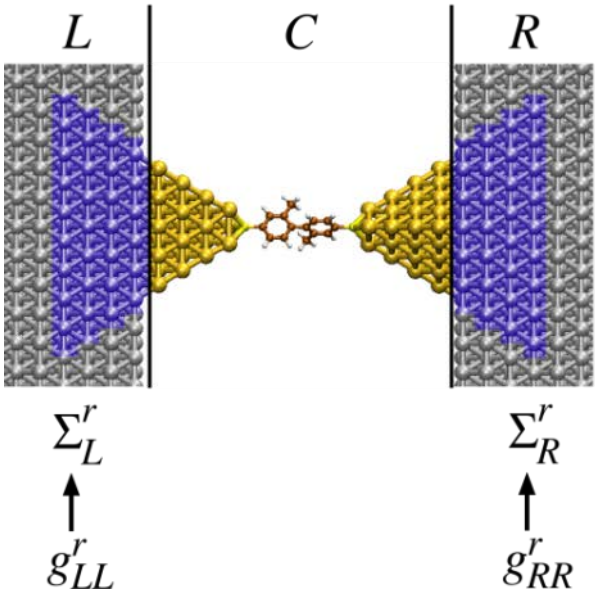
Self energies (X=L,R)

$$\Sigma^r_X = \left(H_{CX} - ES_{CX}\right) g^r_{XX} \left(H_{XC} - ES_{XC}\right)$$

Linewidth broadening matrix $\Gamma_X = -2\,\mathrm{Im}\left[\Sigma^r_X\right]$

Cluster-based ansatz

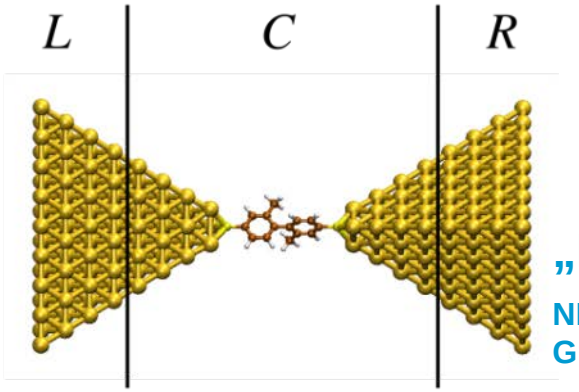
F. Pauly et al., New J. Phys. 2008 ← **Own publications**



S_{CC}, H_{CC}

S_{CL}, H_{CL}

S_{CR}, H_{CR}



S^{ECC}, H^{ECC}

TURBOMOLE@work

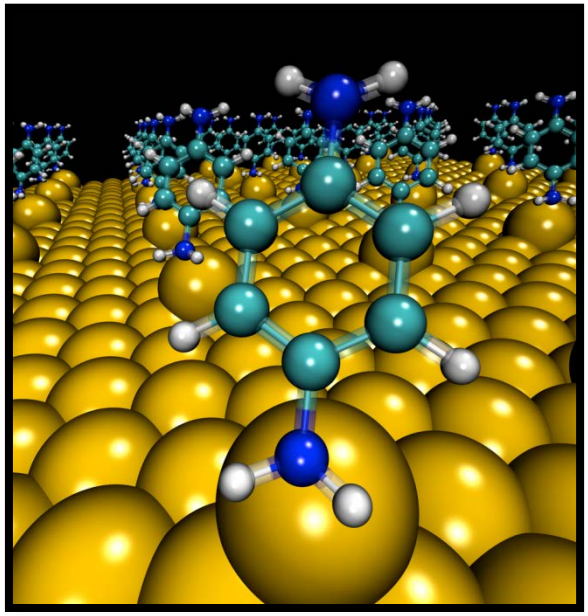
„DFT+NEGF“

NEGF: Nonequilibrium Green‘s functions

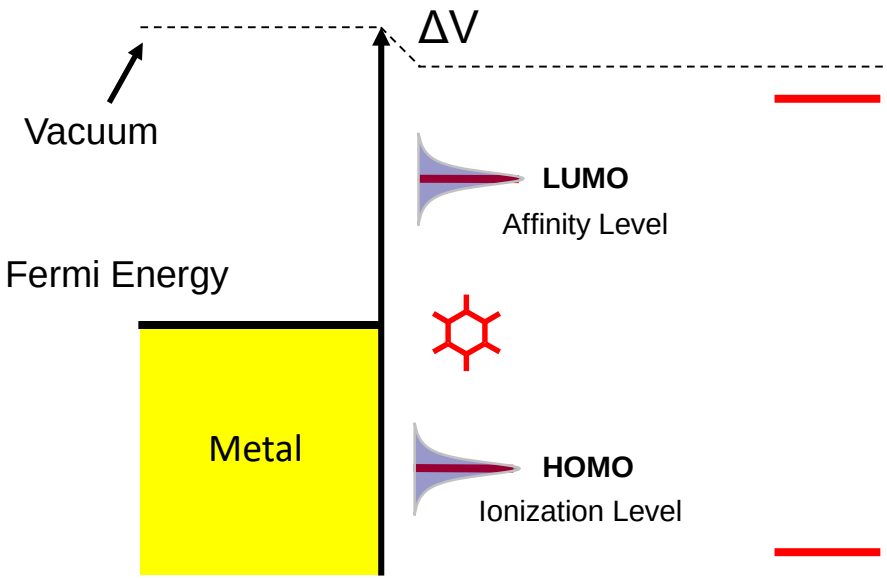
see also M. Brandbyge et al., Phys. Rev. B 65, 165401 (2002)

Level alignment at metal-molecule contact

Metal-molecule contact



Energy level diagram



Physical effects influencing level alignment

- Interfacial charge rearrangement
- Quantum mechanical coupling
- Nonlocal surface polarization

Spectral adjustment: “DFT+Σ“

S. Y. Quek et al., Nano Lett. 7, 3477 (2007)

GW quasiparticle methods

M. Strange et al., Phys. Rev. B 83, 115108 (2011)

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

Hartree-Fock	$\Sigma^{HF}(r,r') = i\hbar G(r,r';-\eta)v(r,r')$
DFT	$\Sigma^{DFT}(r,r') = V_{XC}(r)\delta(r-r')$
GW	$\Sigma^{GW}(r,r';\omega) = \frac{i\hbar}{2\pi}\int_{-\infty}^{\infty} G(r,r';\omega+\omega')W(r,r';\omega')d\omega'$

"HF" in screened Coulomb interaction

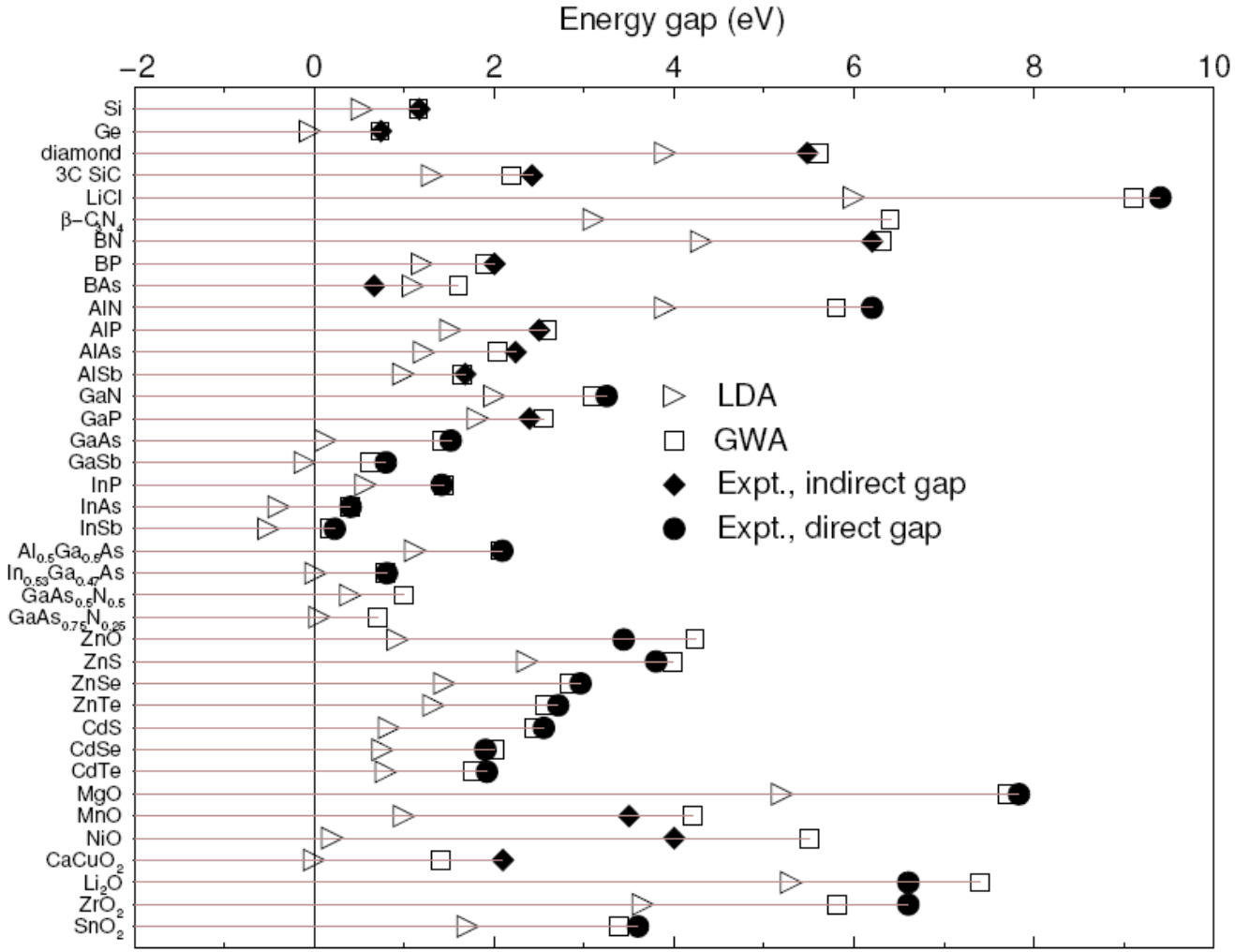
Coulomb interaction $v(r,r') = e^2/(4\pi\varepsilon_0|r-r'|)$

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 $P(r,r';\tau) = -i\hbar G(r,r';\tau)G(r',r;-\tau)$

The „band gap“ problem



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

Phonon dispersion relations

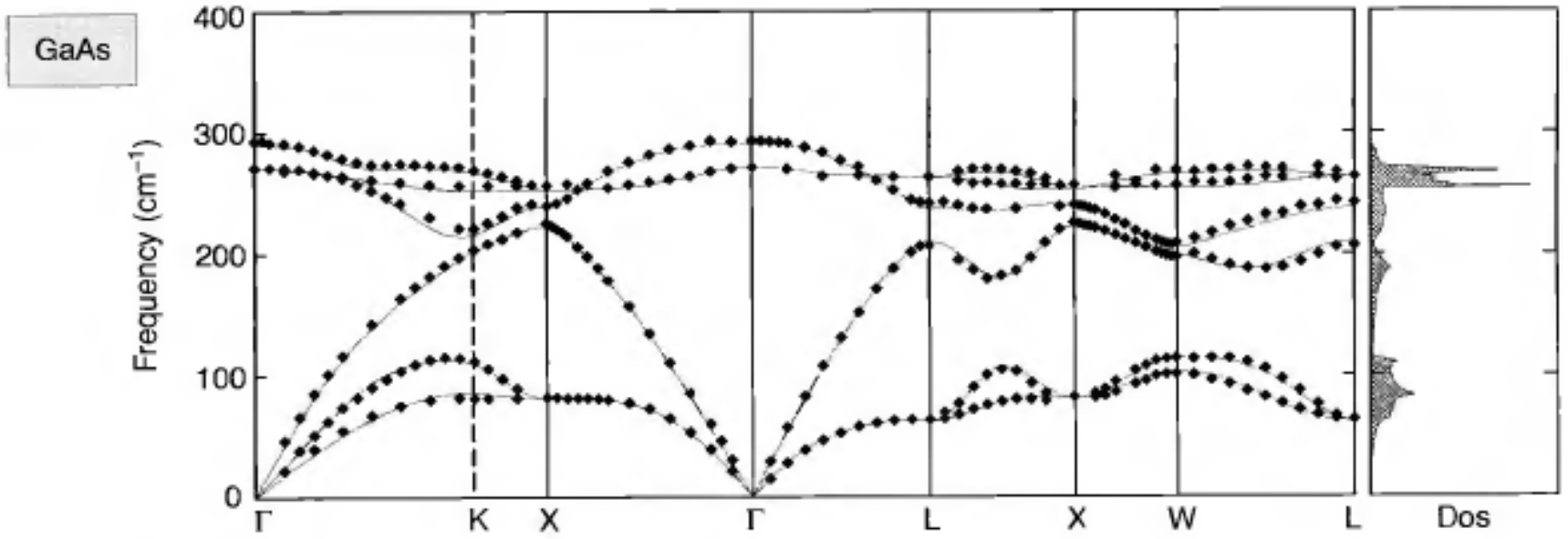


Figure 2.9. Phonon dispersion curves calculated for the semiconductor GaAs [154]. The points are from experiment and the curves from density functional theory using the response function method (Ch. 19). Similar agreement is found for the entire family of semiconductors. Calculations for many types of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

R. M. Martin, Electronic Structure, Cambridge University Press, 2008

Spring constants needed $K_{i\mu,j\nu} = \dfrac{\partial^2 E}{\partial R_{i\mu}\partial R_{j\nu}}$

➡ Phonon or lattice heat transport

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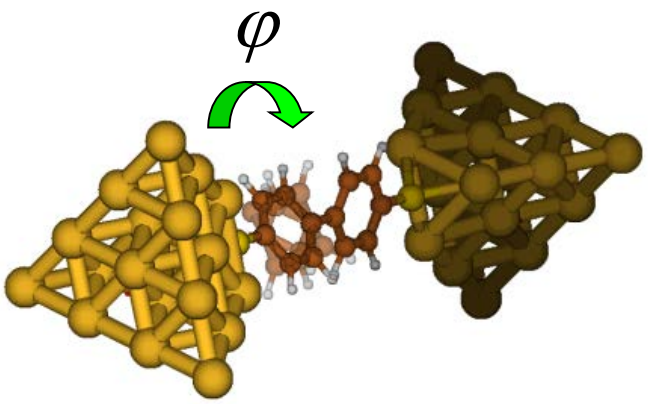
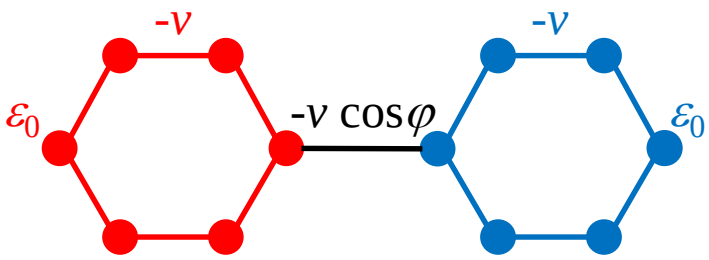
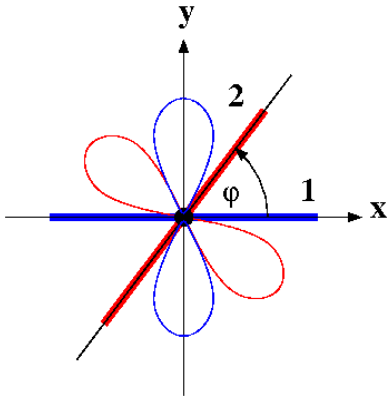
Summary & outlook

Structure-conductance relationships



What is the influence of conjugation on molecular conductance?



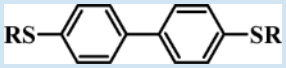
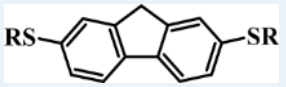
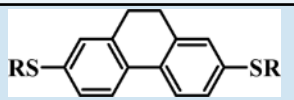
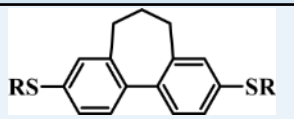
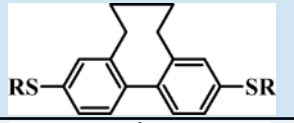
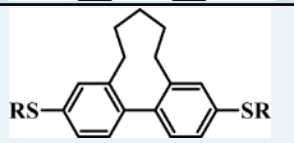
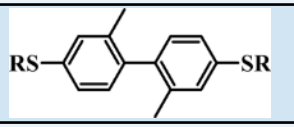
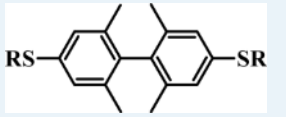


Transition amplitude between rings $\propto \cos\varphi$

Transmission or conductance: $G \propto \cos^2 \varphi$

Influence of conjugation on conductance

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

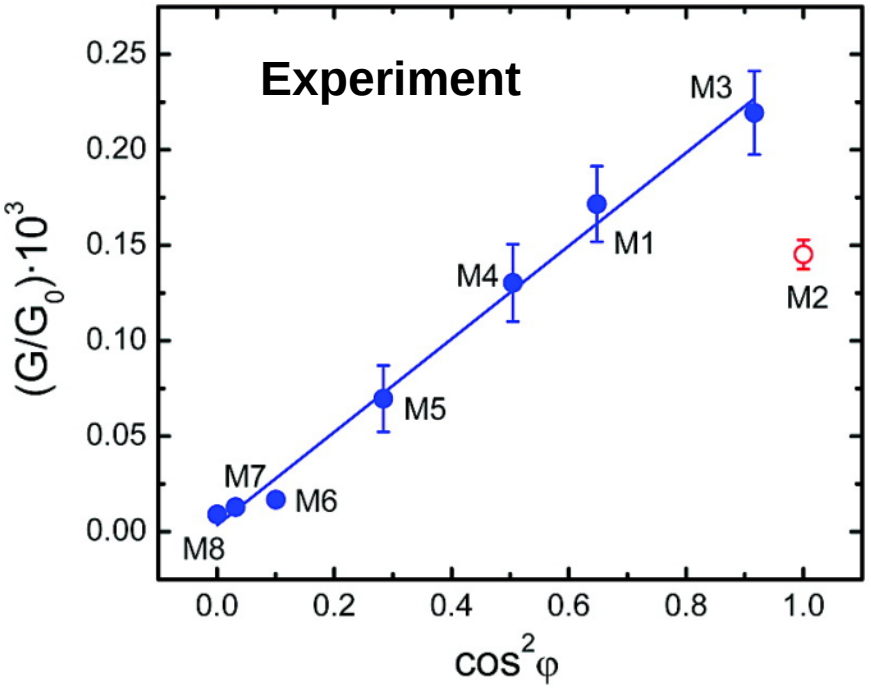
Molecule	Structure	Torsion angle φ (X-Ray, Acetyl)
M1		36.4°
M2		1.1°
M3		16.8°
M4		44.7°
M5		57.8°
M6		71.5°
M7		79.7°
M8		89.0°

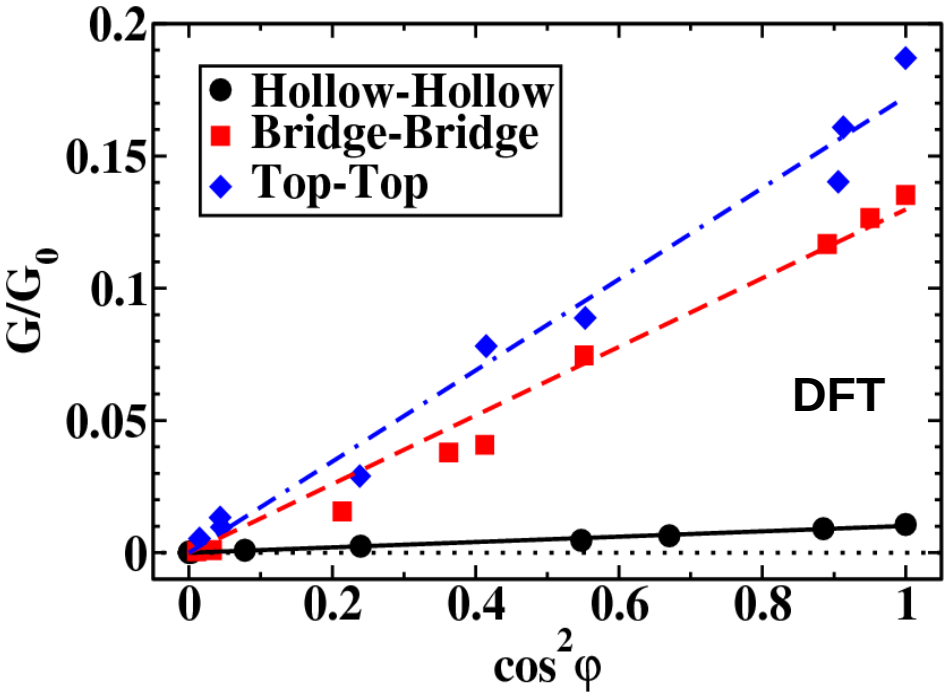
Tailor-made side groups gradually change the torsion angle

See also:
L. Venkataraman et al., Nature 442, 904 (2006)

Influence of conjugation on conductance

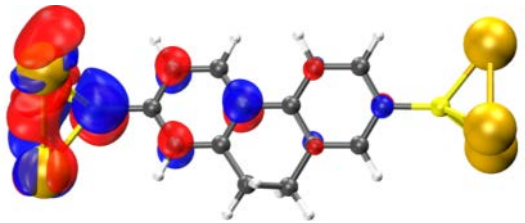
A. Mishchenko et al., Nano Lett. **10**, 156 (2010)





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

M. Bürkle et al., Phys. Rev. B 85, 075417 (2012)

Green's function formalism

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- Heat dissipation

Summary & outlook

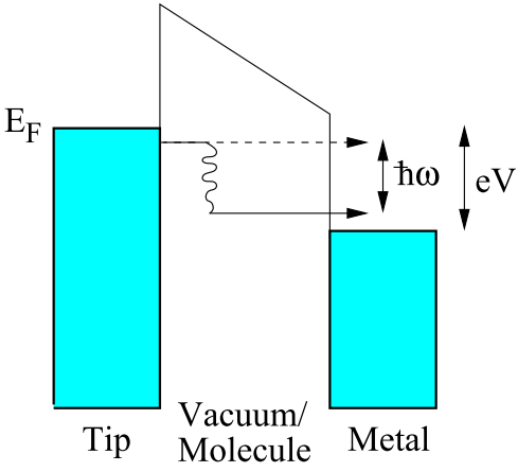
Inelastic interactions due to vibrations

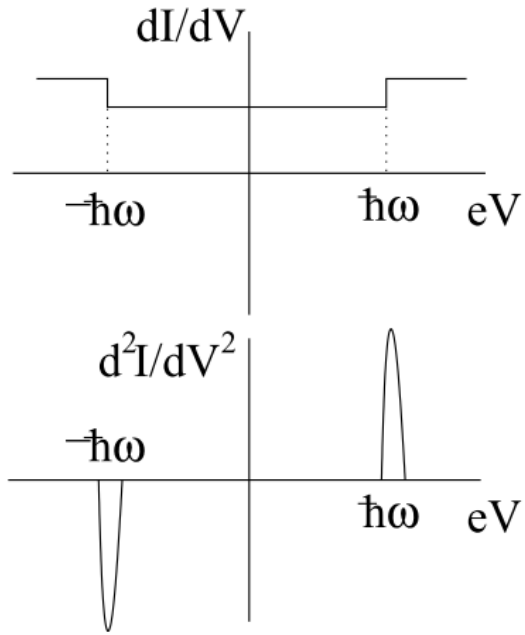
Is there a molecule in the contact?
→ Vibrations yield a fingerprint

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. K. Viljas et al., Phys. Rev. B 72, 245415 (2005)
T. Frederiksen et al., Phys. Rev. B 75, 205413 (2007)
J. C. Cuevas and E. Scheer, *Molecular Electronics*, World Scientific (2010)

Inelastic transport method

$$H = H_e + H_{vib} + H_{e-vib};\ H_e = \sum_{i,j} d_i^\dagger H_{ij} d_j;\ H_{vib} = \sum_\alpha \hbar\omega_\alpha b_\alpha^\dagger b_\alpha;\ H_{e-vib} = \sum_{i,j}\sum_\alpha d_i^\dagger \lambda_{ij}^\alpha d_j \left(b_\alpha^\dagger + b_\alpha\right)$$

$$\lambda_{ij}^\alpha = \sqrt{\frac{\hbar}{2\omega_\alpha}} \sum_{k,\mu} \left\langle i \middle| \nabla_{k\mu} H_e \middle|_{\vec{Q}=0} \middle| j \right\rangle A_{k\mu,\alpha}$$

→ 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

$$I = I_{el} + \delta I_{el} + I_{inel}$$

$$I_{el} = \frac{2e}{h}\int \mathrm{d}E \mathrm{Tr}[\boldsymbol{G}^r \boldsymbol{\Gamma}_R \boldsymbol{G}^a \boldsymbol{\Gamma}_L]\left(f_L - f_R\right)$$

$$\delta I_{el} = \frac{4e}{h}\int \mathrm{d}E \mathrm{ReTr}[\boldsymbol{\Gamma}_L \boldsymbol{G}^r \boldsymbol{\Sigma}^r_{e\text{-vib}} \boldsymbol{G}^r \boldsymbol{\Gamma}_R \boldsymbol{G}^a]\left(f_L - f_R\right)$$

$$I_{inel} = -\mathrm{i}\frac{2e}{h}\int \mathrm{d}E \mathrm{Tr}\left[\boldsymbol{G}^a \boldsymbol{\Gamma}_L \boldsymbol{G}^r \left\{\left(f_L - 1\right)\Sigma^<_{e-vib} - f_L \Sigma^>_{e-vib}\right\}\right]$$

Transport theory: J. K. Viljas et al., Phys. Rev. B 72, 245415 (2005)
M. Bürkle et al., Phys. Status Solidi B 250, 2468 (2013)

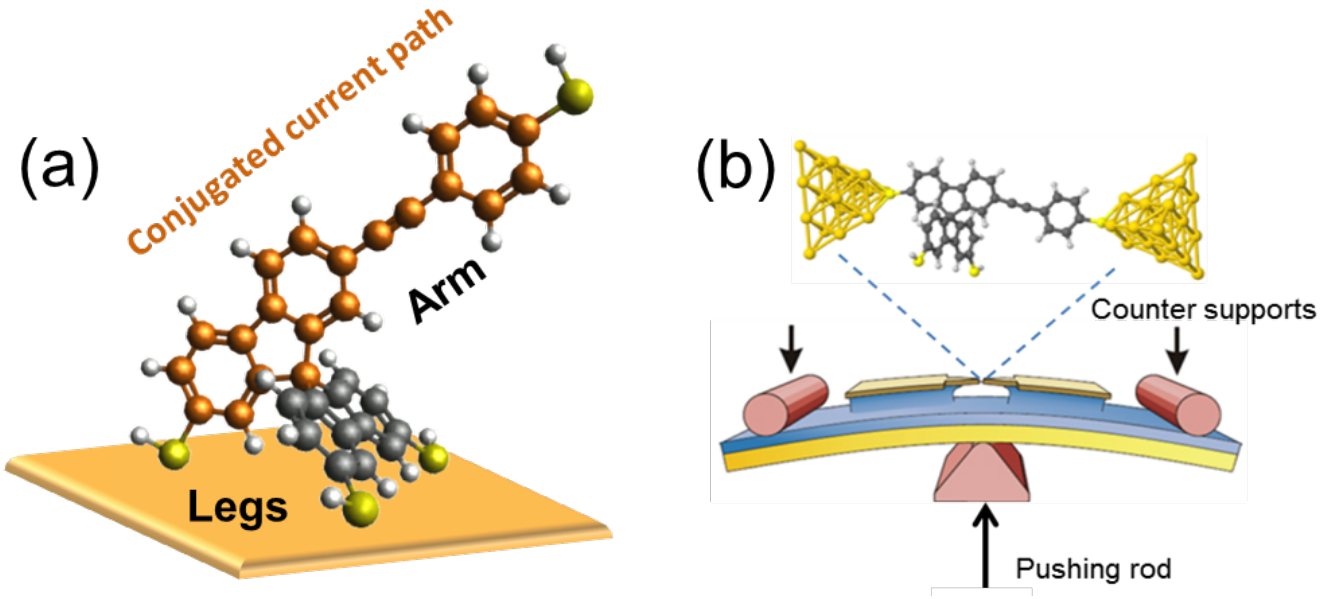
Molecules on surfaces

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

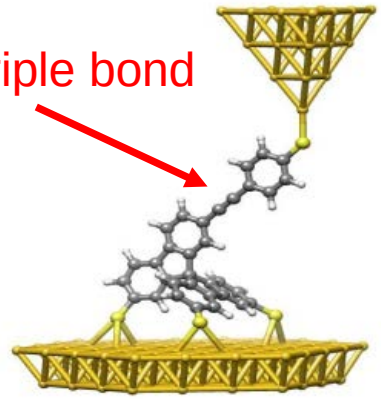
Is the molecule positioned on the surface as intended, and how does the current proceed?



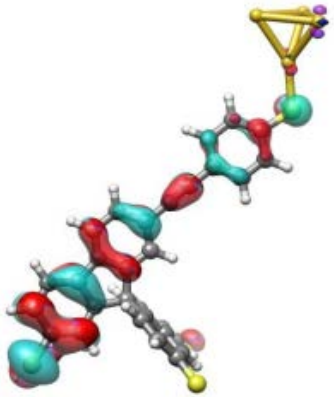
M. A. Karimi et al., Nanoscale 8, 10582 (2016)

Related STM study: L. Gerhard et al, under review in Nature Comm.

Current path for a conductive molecular wire on a tripodal platform



Conduction eigenchannel

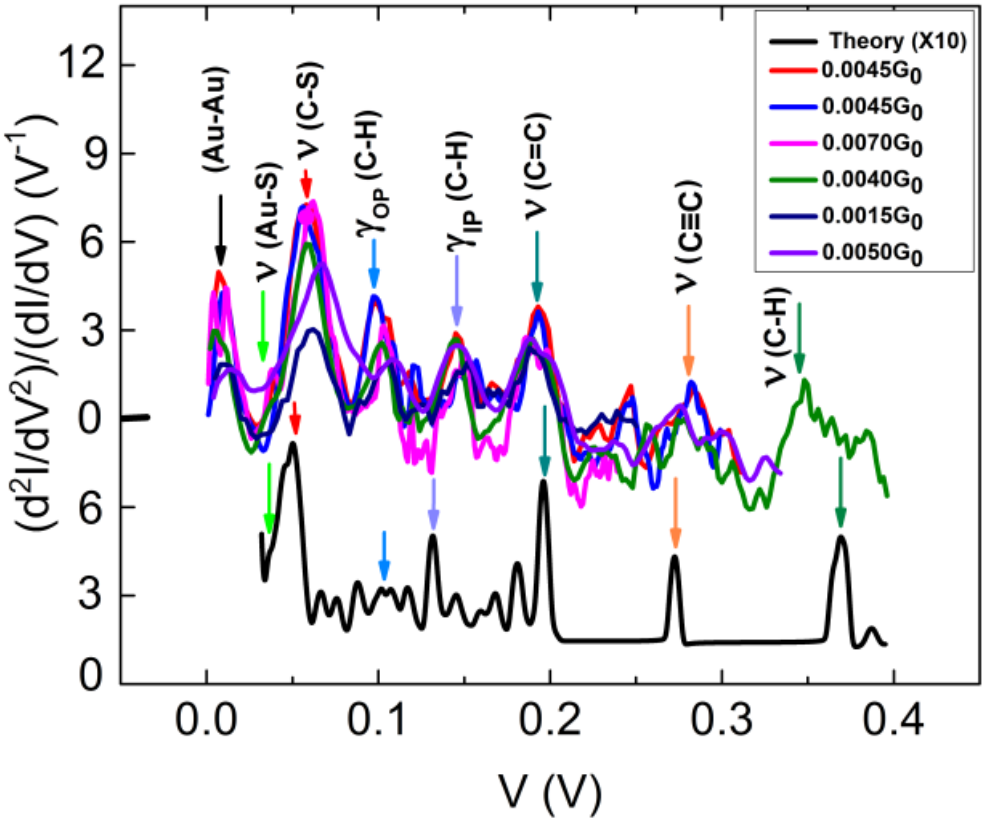


Theory: DFT+Σ

- Elastic transmission agrees with average experimental conductance, $G \approx 10^{-3} G_0$

→ indicates right junction geometry

- Inelastic tunneling spectra confirm transport through backbone



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

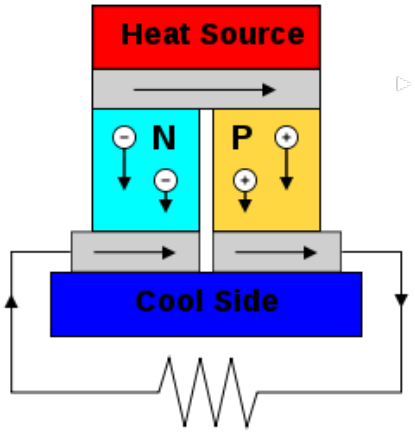
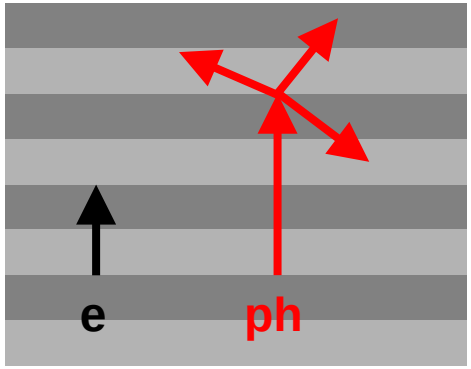


Figure of merit characterizes thermoelectric power generation efficiency: $ZT=S^2GT/\kappa$

Thermopower S
Electric conductance G
Temperature T
Thermal conductance κ

$$\kappa = \kappa_{el} + \kappa_{ph}$$



Electron & phonon transport

➡ Enhancement of ZT through appropriate nanostructuring

How large is ZT for molecular junctions?
How do κ_{el} and κ_{ph} compare?

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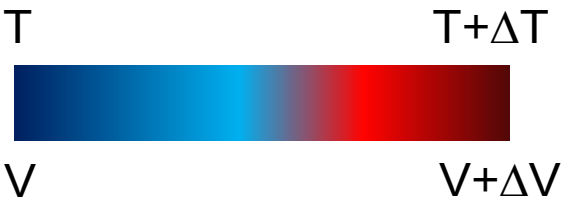
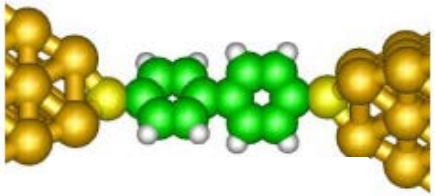
  - Thermopower
  - Phonon thermal transport
  - Figure of merit
- Heat dissipation

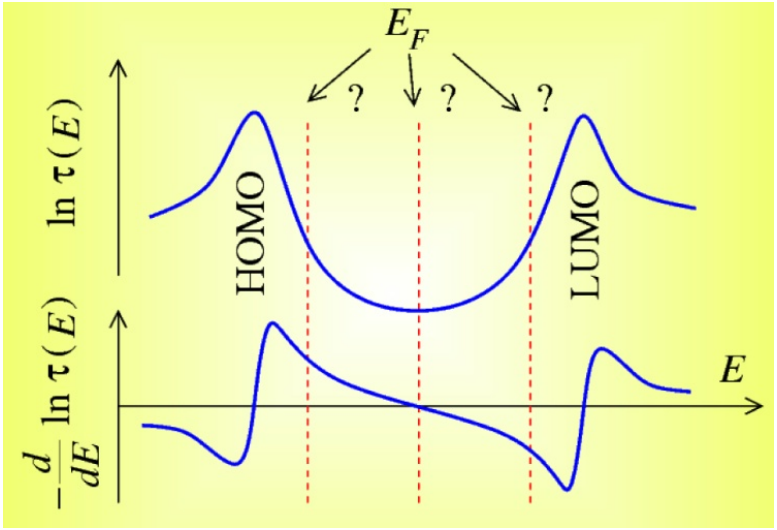
Summary & outlook

Why thermopower?

Seebeck effect







Landauer-Büttiker formalism

Thermopower (electronic contribution):

$$S = -\left.\frac{\Delta V}{\Delta T}\right|_{I=0} \approx -\frac{\pi^2 k_B}{3e} k_B T \left.\frac{\partial \ln(\tau(E))}{\partial E}\right|_{E=E_F}$$

- Sign of *S* distinguishes "*electron* type" and „*hole* type" conduction

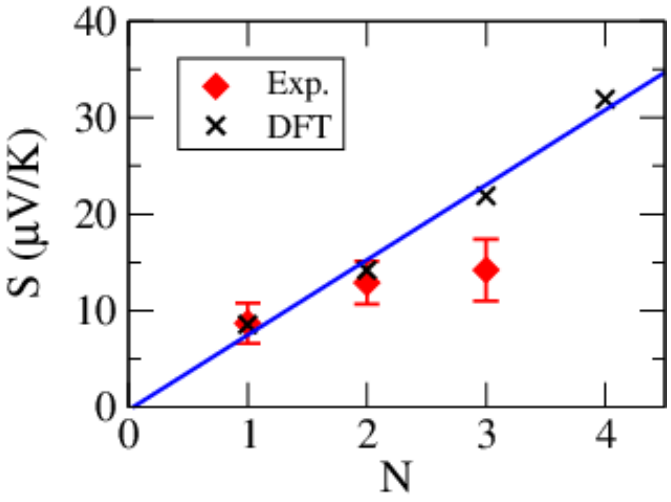
→ Hint to position of E_F with respect to HOMO and LUMO

Theory suggestion
M. Paulsson et al., Phys. Rev. B 67, 241403(R) (2003)

First experiment
P. Reddy et al., Science 315, 1568 (2007)

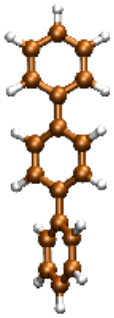
Theoretical studies of the thermopower

Theory: DFT



Length dependence

N=3

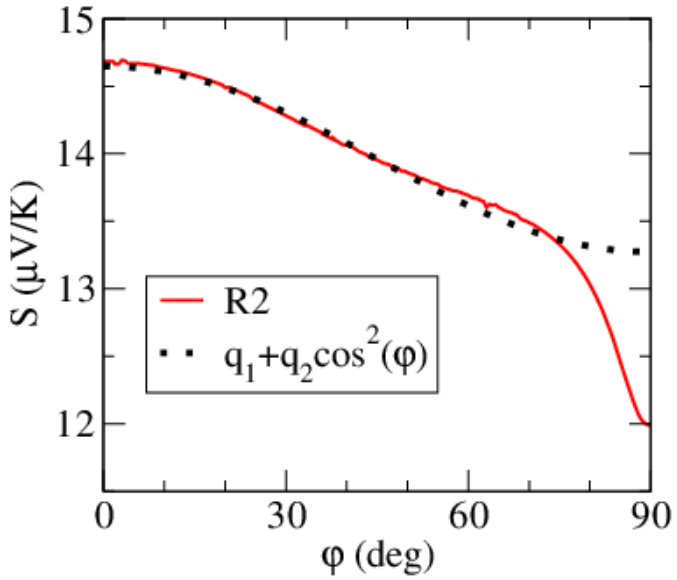


$$\tau(E) \approx \alpha(E)\exp(-\beta(E)N)$$

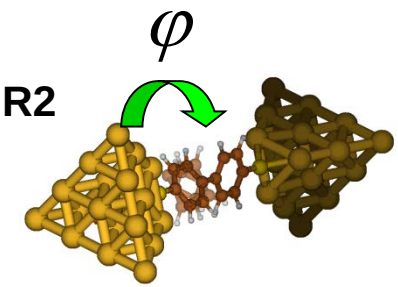
$$S = S^{(0)} + S^{(1)}N$$

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

Exp.: P. Reddy et al., Science 315, 1568 (2007)
Theory: F. Pauly et al., Phys. Rev. B 78, 035315 (2008)



Influence of conjugation



Change of conjugation leads only to slight variation of thermopower

F. Pauly et al., Phys. Rev. B 78, 035315 (2008)
M. Bürkle et al., Phys. Rev. B 86, 115304 (2012)

Metallic atomic contacts

F. Pauly et al., Phys. Rev. B 84, 195420 (2011)
C. Evangeli et al., Nano Lett. 15, 1006 (2015)

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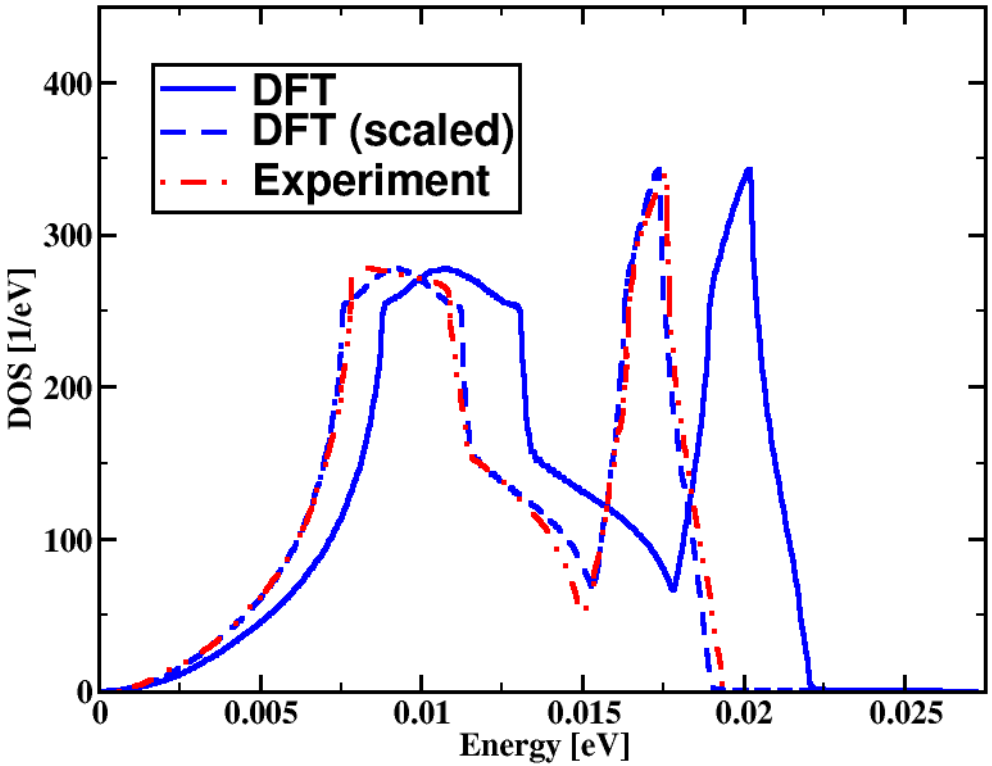
  - Phonon thermal transport
  - Figure of merit
- Heat dissipation

Summary & outlook

Phonon thermal transport

Phonon density of states of bulk gold

- Extracted from finite clusters
- Good agreement with experiment



M. Bürkle et al., Phys. Rev. B 91, 165419 (2015)

Force constant matrix

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

Phonon transmission

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

$$H \to K; E \to E^2$$

Linear response properties

Phonons: $$\kappa_{ph} = \frac{1}{h} \int_0^\infty dE \tau_{ph}(E) \frac{\partial n}{\partial T} E$$

Electrons: $G = G_0 K_0$ $\quad S = -\frac{K_1}{eTK_0}$

$$\kappa_{el} = \frac{2}{hT} \left(K_2 - \frac{K_1^2}{K_0} \right)$$

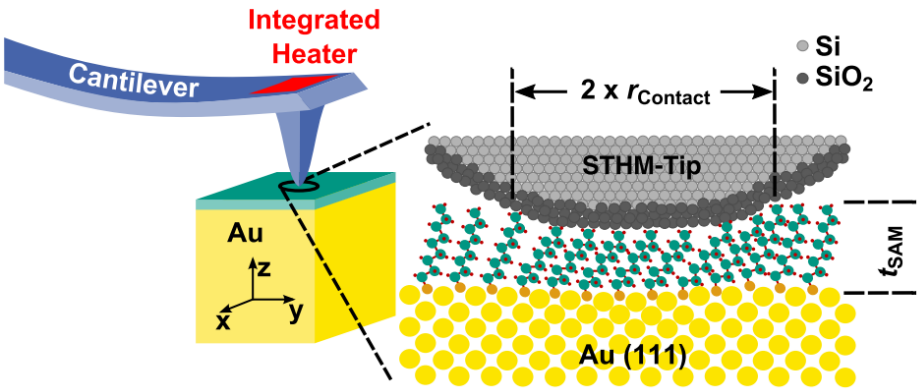
$$K_n = \int dE \tau_{el}(E) \left(-\frac{\partial f}{\partial E} \right) (E - \mu)^n$$

Heat transport at the nanoscale

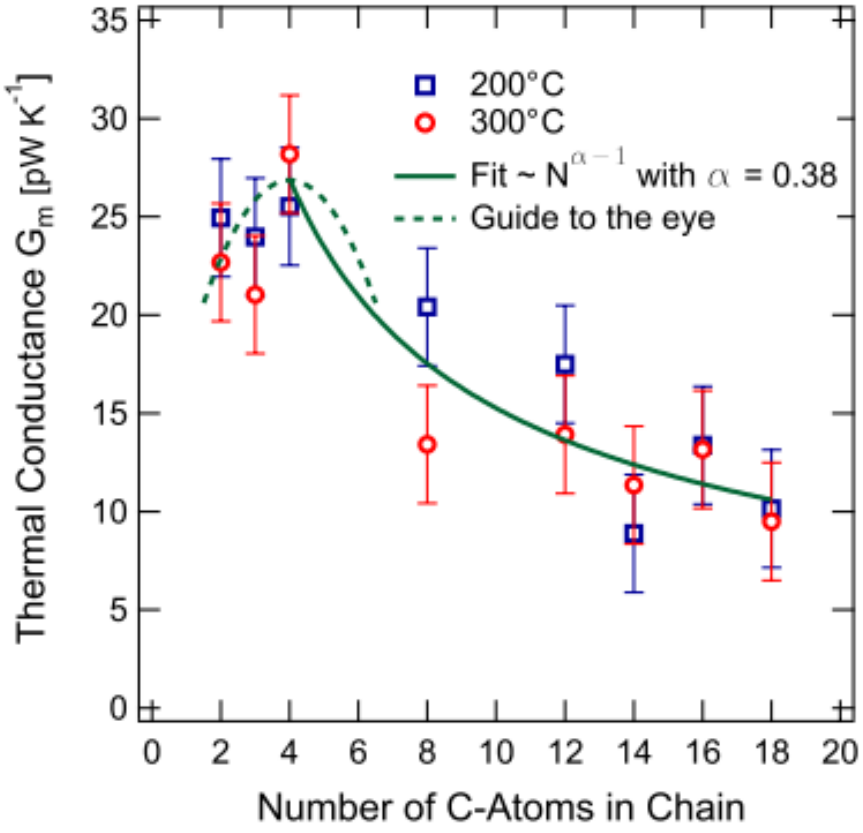
Growing interest in heat transport at the nanoscale
Goal: Transfer knowledge on nanoelectronics to nanophononics

State of the art – Experiments

– Experiments with SAMs show chemical sensitivity (length, anchoring groups, …)



IBM Zurich:
T. Meier et al., Phys. Rev. Lett. 113, 060801 (2014)



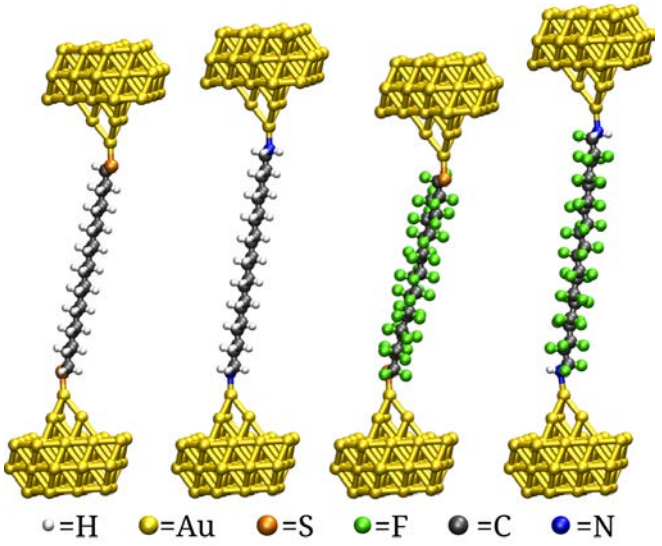
→ Single-molecule sensitivity is a goal of several experimental groups

Length dependence of the thermal conductance

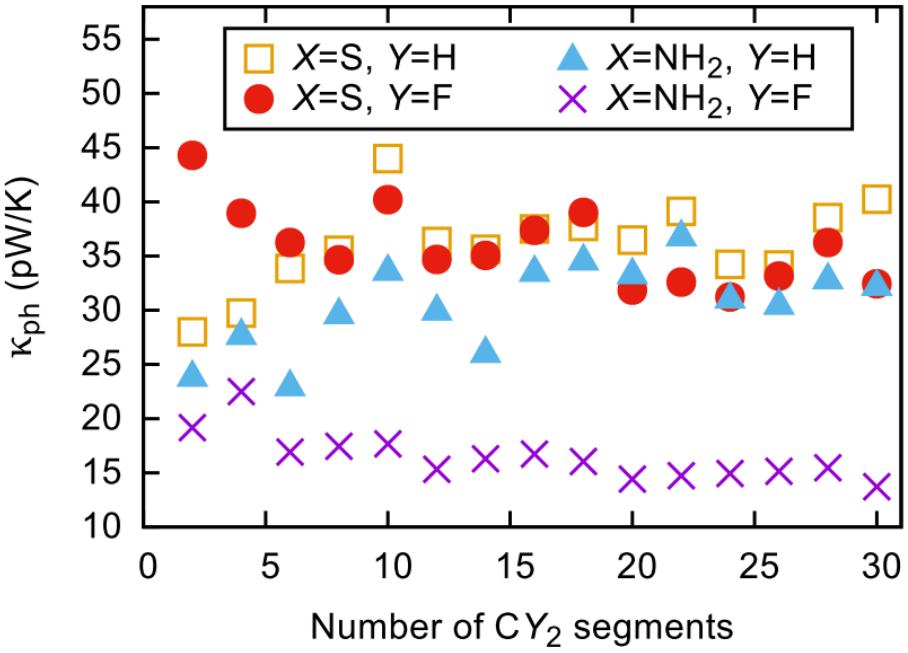
Alkane single-molecule junctions

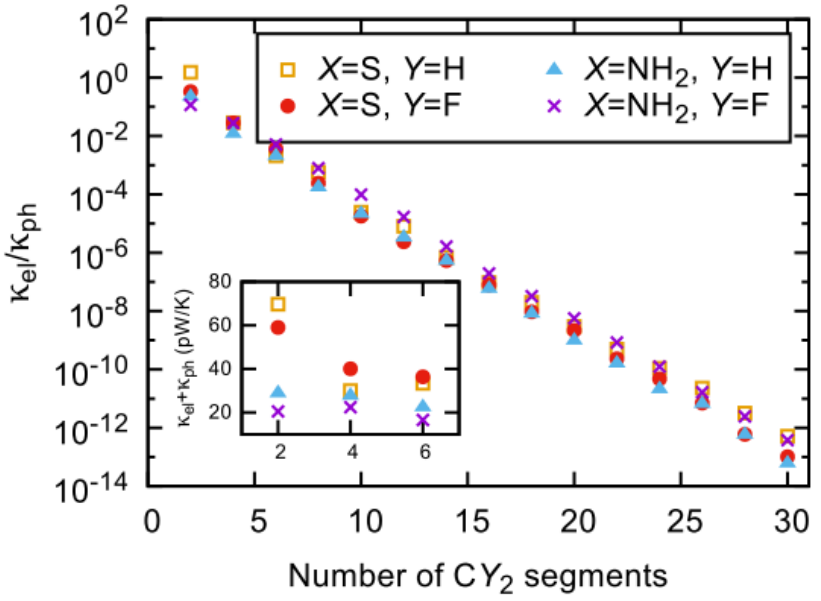
- Chains with 2 to 30 units
- Units CY_2 with Y=H or F
- Anchor group X=S or NH_2

→ Thermal conductance rather length-independent for 5 or more CY_2 units



J. C. Klöckner et al., arXiv:1609.03827





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  - Figure of merit
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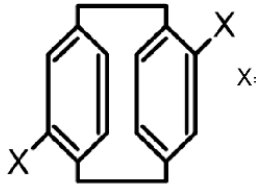
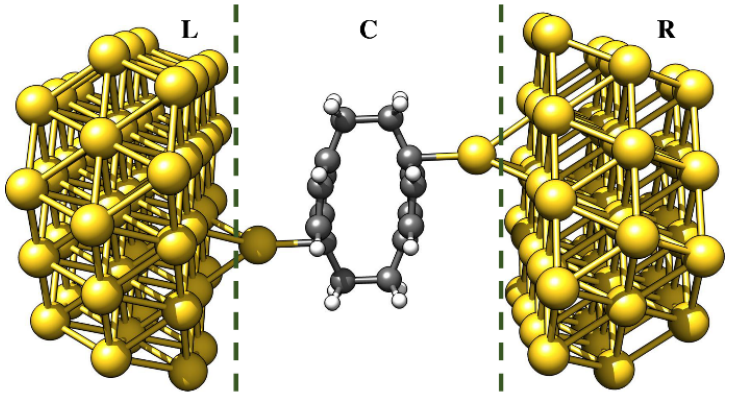
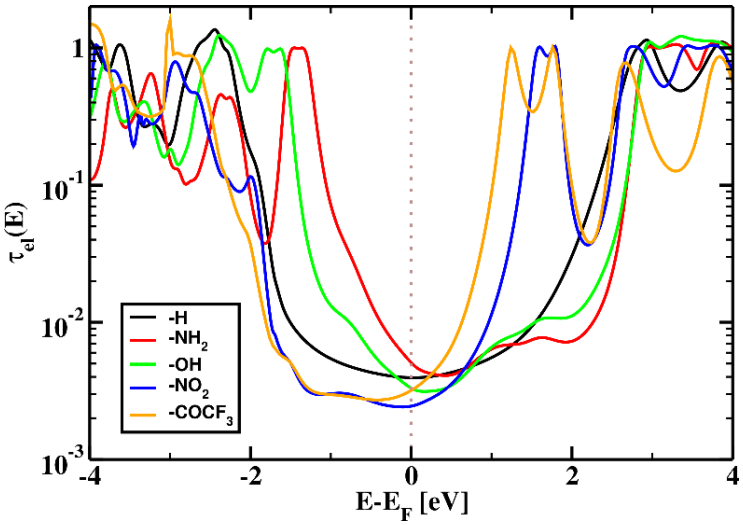
Summary & outlook

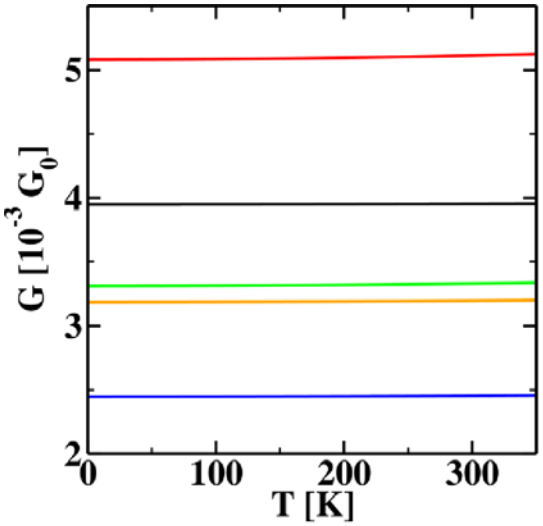
Figure of merit without phonon thermal transport

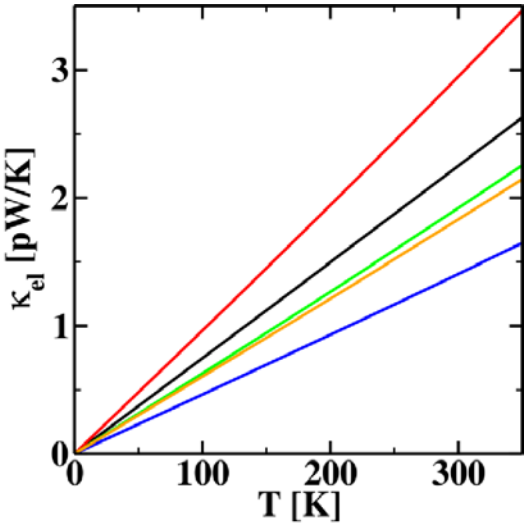
Theory: DFT+Σ

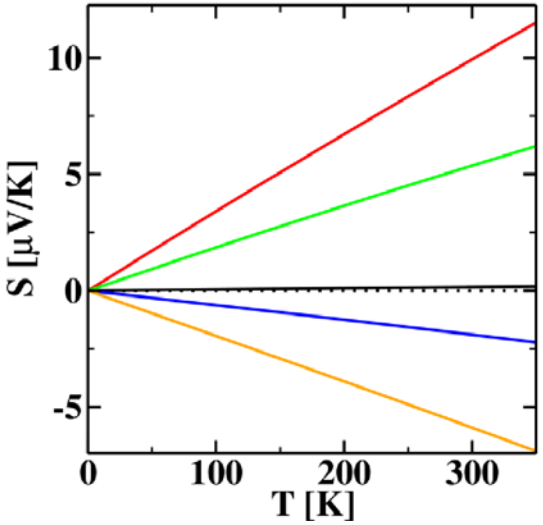












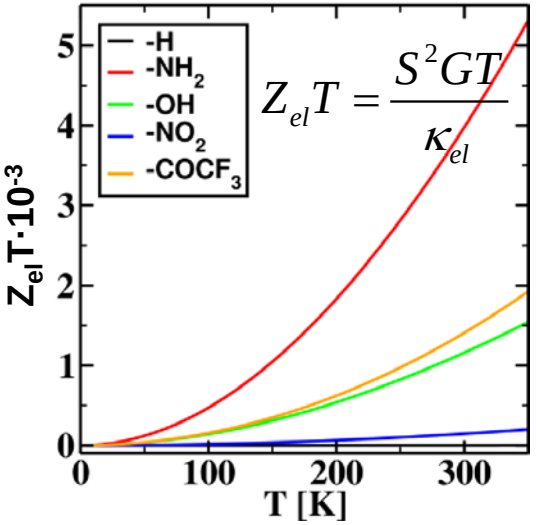
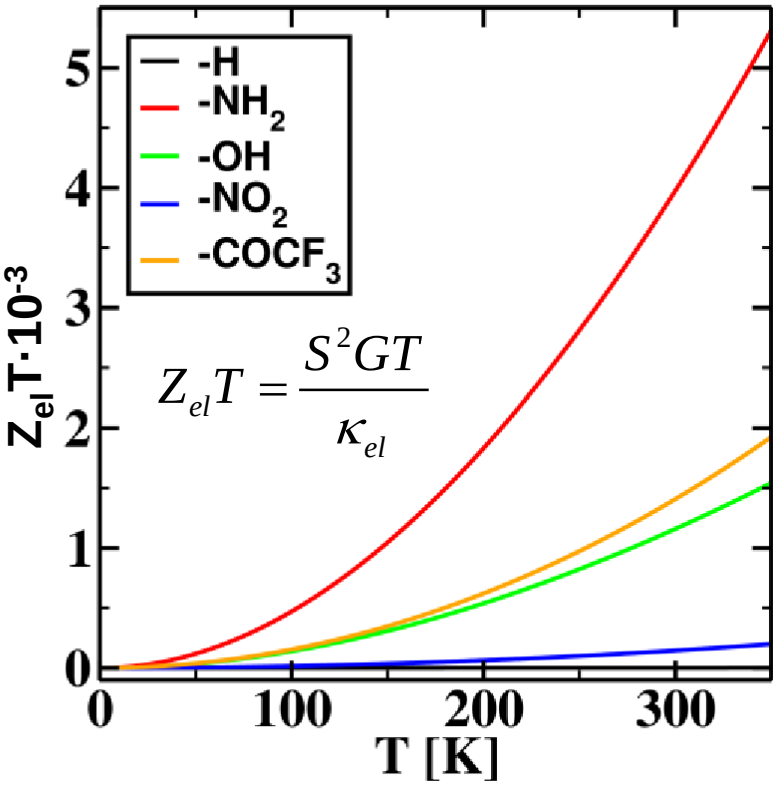
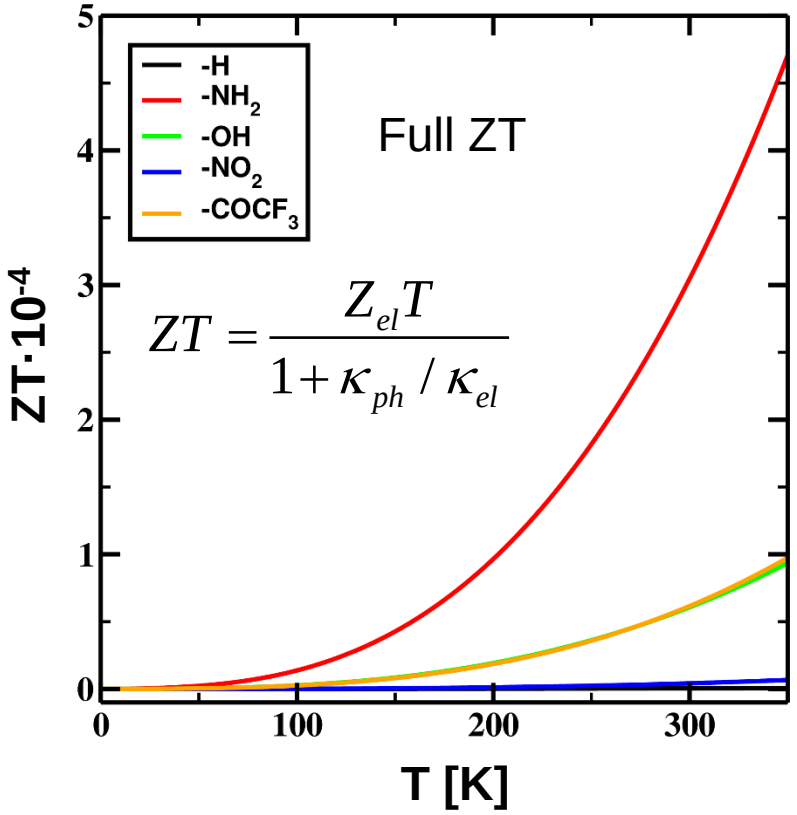


Figure of merit including phonon thermal transport

- κ_{ph} cannot be ignored for realistic estimate of ZT

M. Bürkle et al., Phys. Rev. B 91, 165419 (2015)





Theory: DFT+Σ

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

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

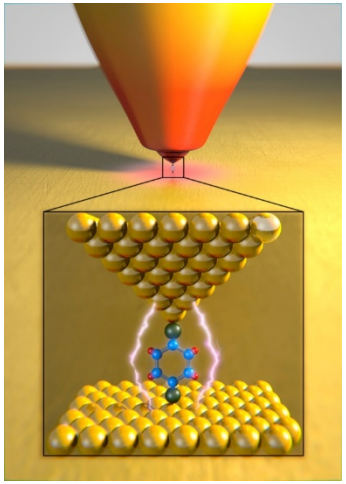
Electrical properties

- Structure-conductance relationships
- Inelastic effects due to vibrations

Beyond electric conductance

- Thermoelectric properties
- Heat dissipation

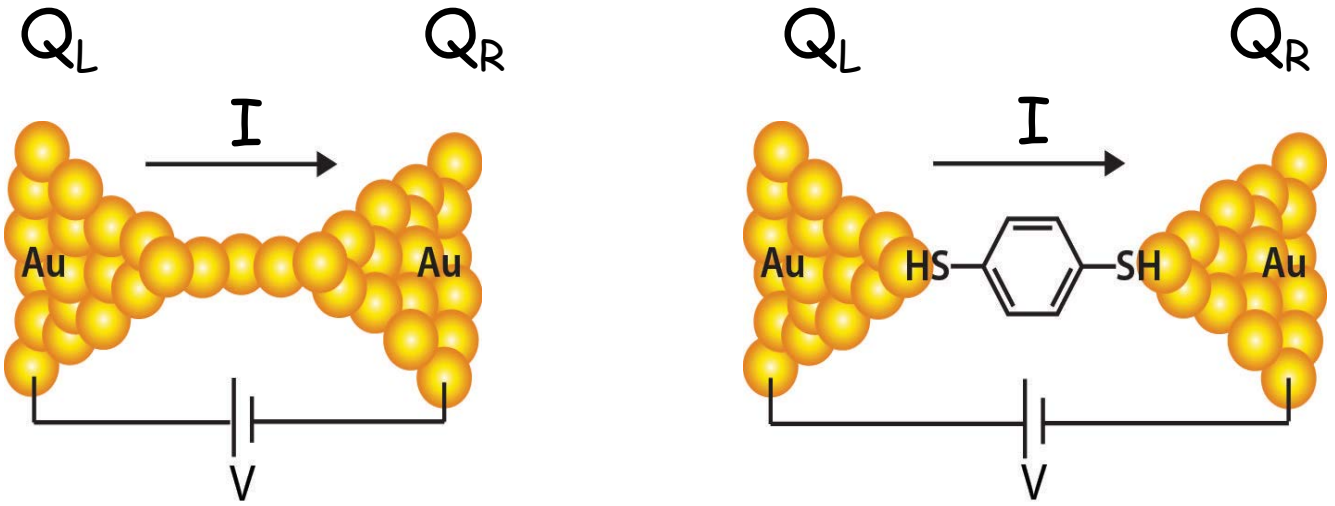
Summary & outlook



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.

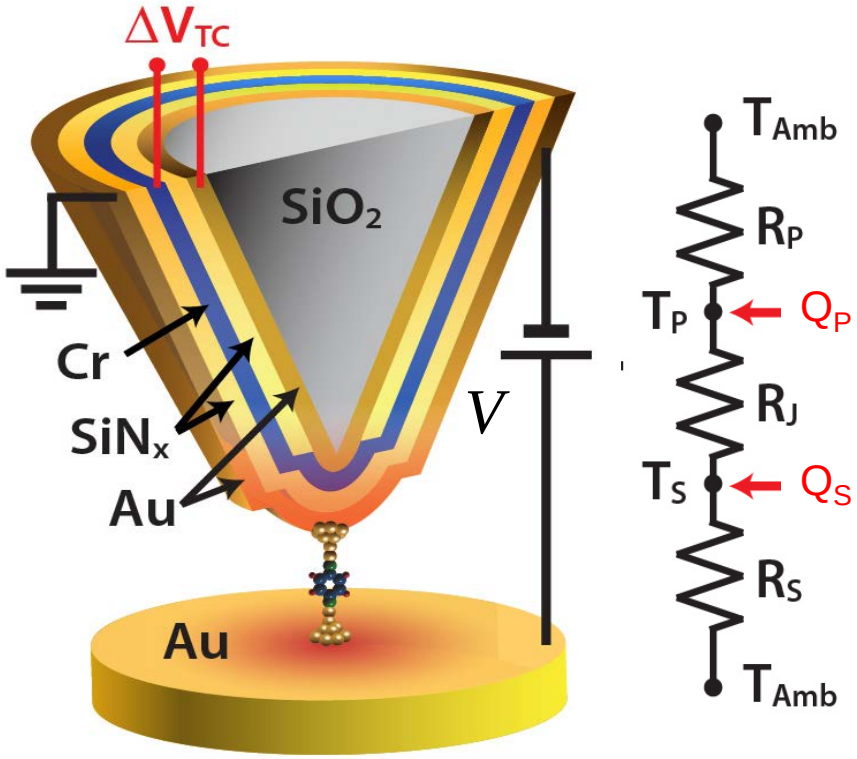


Is the heat dissipated equally in both electrodes?
What is the relation between the dissipated heat and electronic structure?

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

L. A. Zotti et al., New J. Phys. 16, 015004 (2014)

Probing heat dissipation



$R_{J,P,S}$: Thermal resistance of junction, probe, substrate

$R_J \gg R_P, R_S$

$$\Delta V_{TC} = -S_{TC} \times \Delta T_{TC}$$

Thermovoltage Thermopower Temperature rise

$$T_P = T_{Amb} + \Delta T_{TC}$$

$$Q_P(V) = \Delta T_{TC} / R_P$$

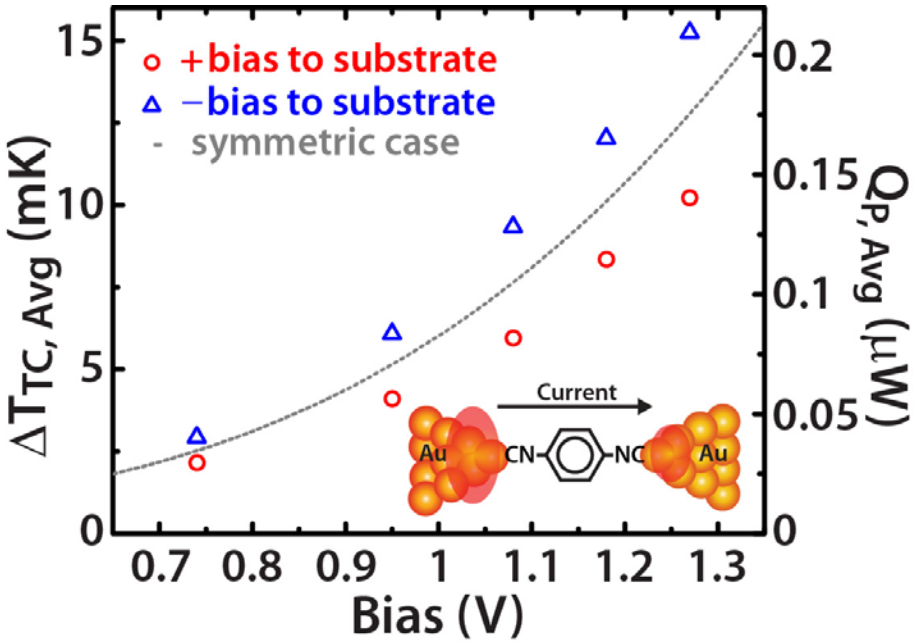
Power dissipation

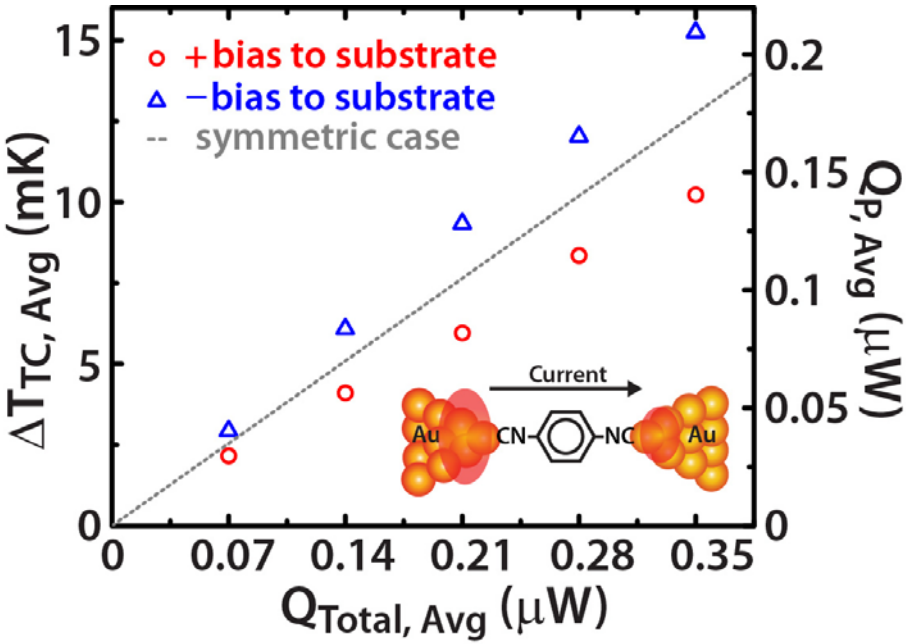
$$Q_P(V) + Q_S(V) = Q_{Total}(V) = I \times V$$

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?

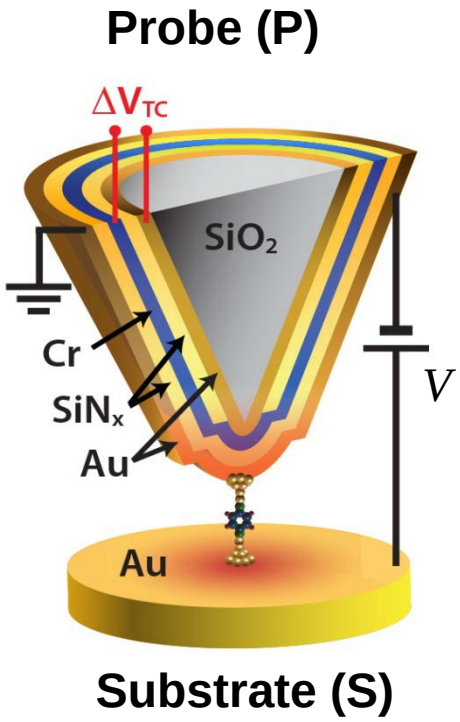
Landauer theory of heat dissipation

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?

$$Q_P(V) = Q_S(V), \quad \text{if} \quad \tau(E,V) = \tau(-E,V)$$

Electron-hole symmetry implies equal dissipation

When is the power dissipation independent of bias polarity?

$$Q_P(V) = Q_P(-V), \quad \text{if} \quad \tau(E,V) = \tau(-E,-V)$$

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

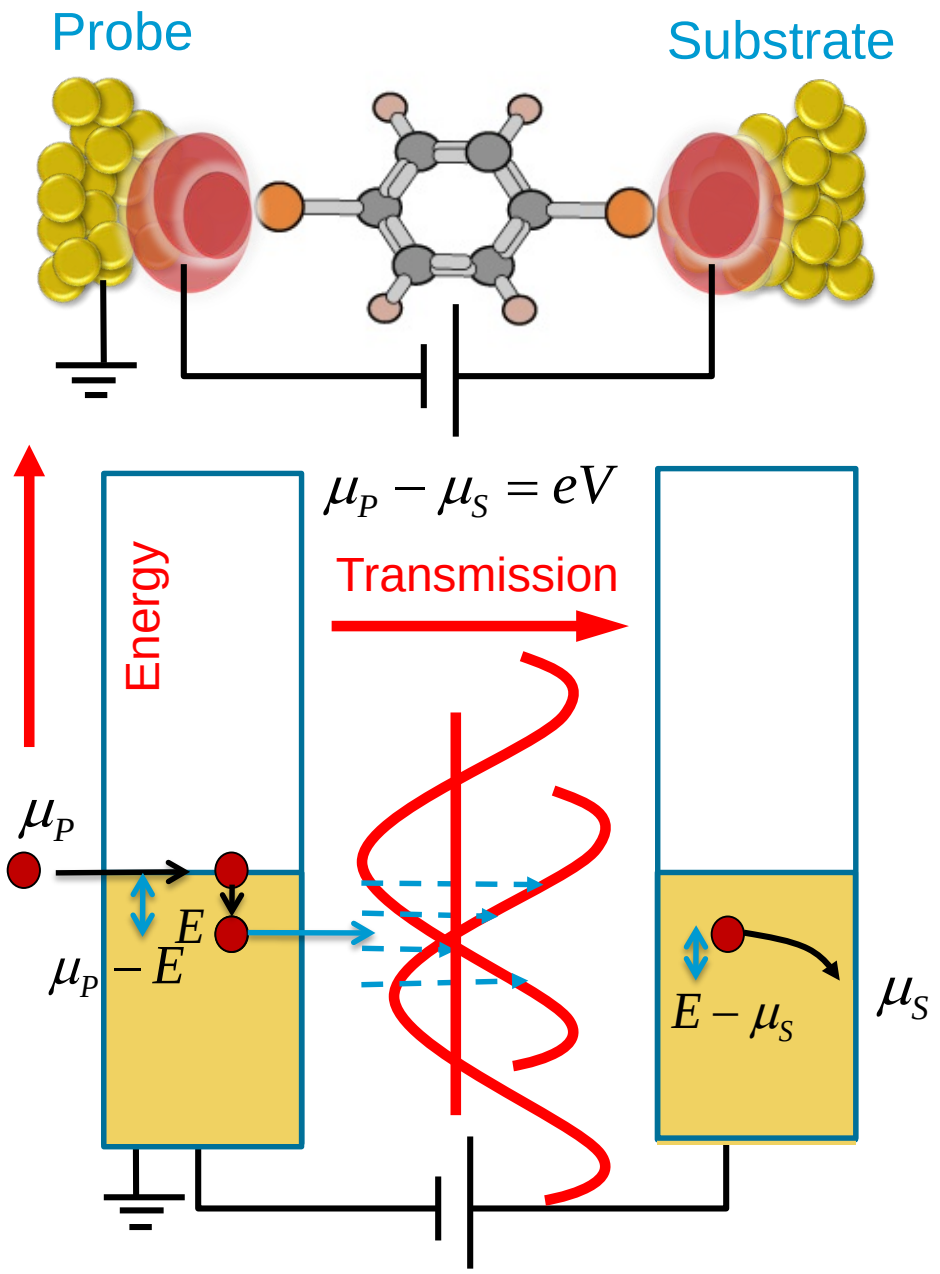
Heating asymmetry should change sign, if sign of S is changed.

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

Asymmetric heat dissipation: simple picture

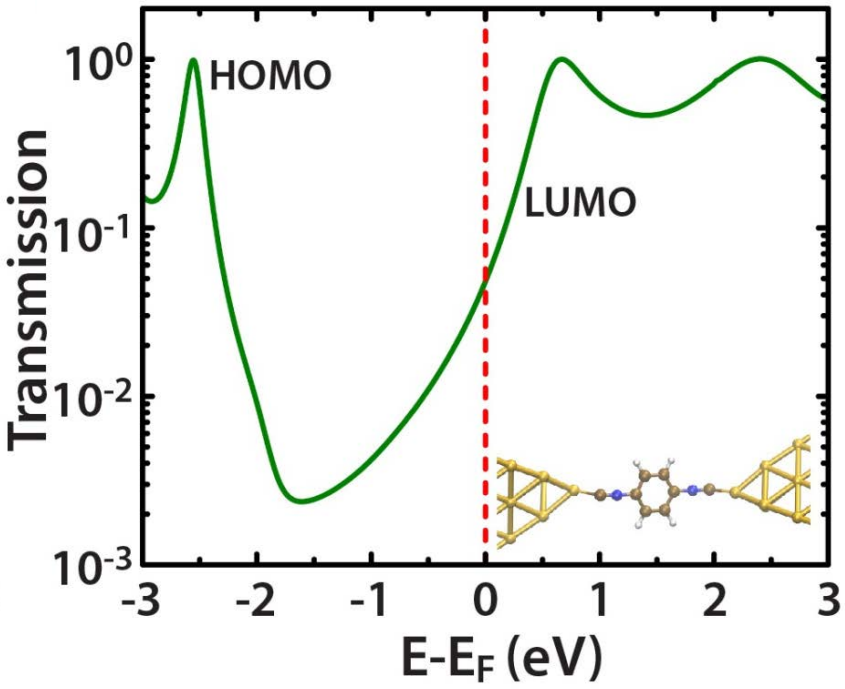
- An electron flows elastically through the contact with energy *E,* leaving a hole behind.
- The electron thermalizes and dissipates an energy (E-μ_S) in the substrate.
- The hole left in the probe is filled by an electron releasing an energy (μ_P-E) in the probe.
- For hole conduction, the heating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

→ **An energy-dependent transmission leads to asymmetric heating.**

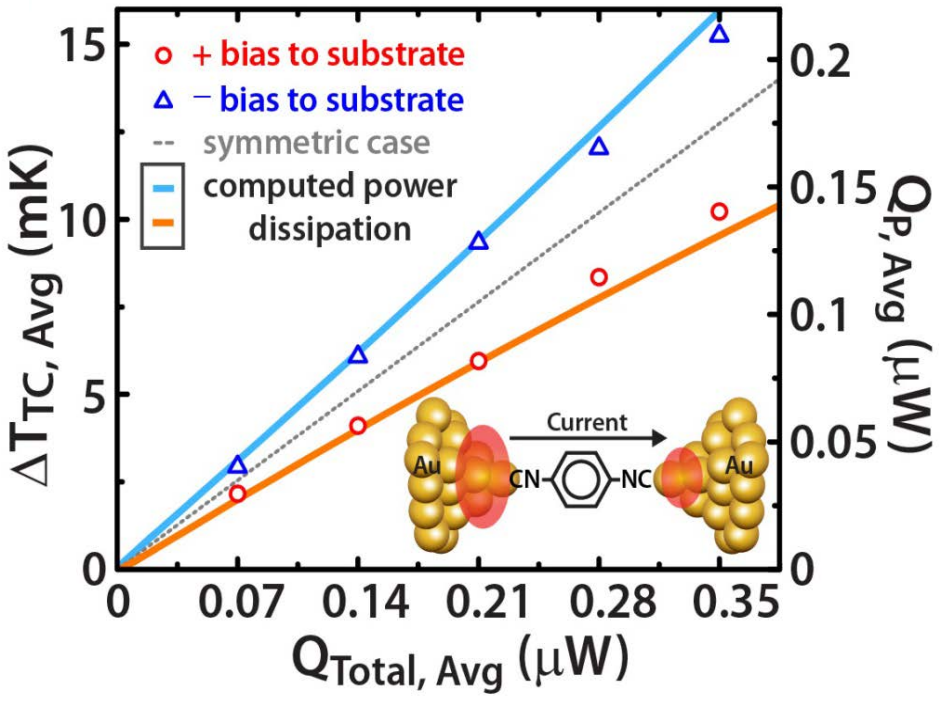


Benzenediisonitrile (BDNC) single-molecule junctions: Comparison between theory & experiment

DFT + NEGF



Power Dissipation



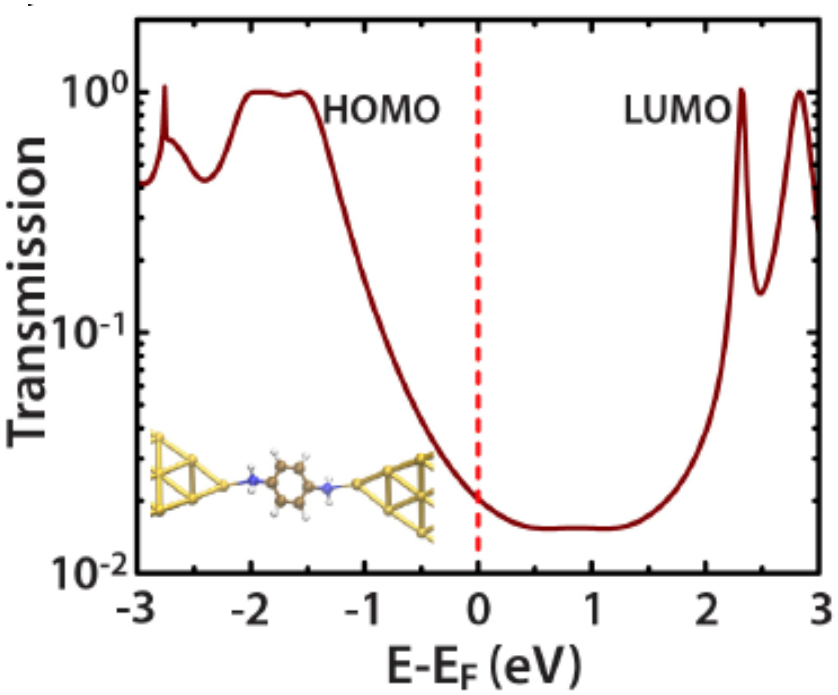
CN-anchors lead to electron conduction

→ Power dissipation higher for negative bias

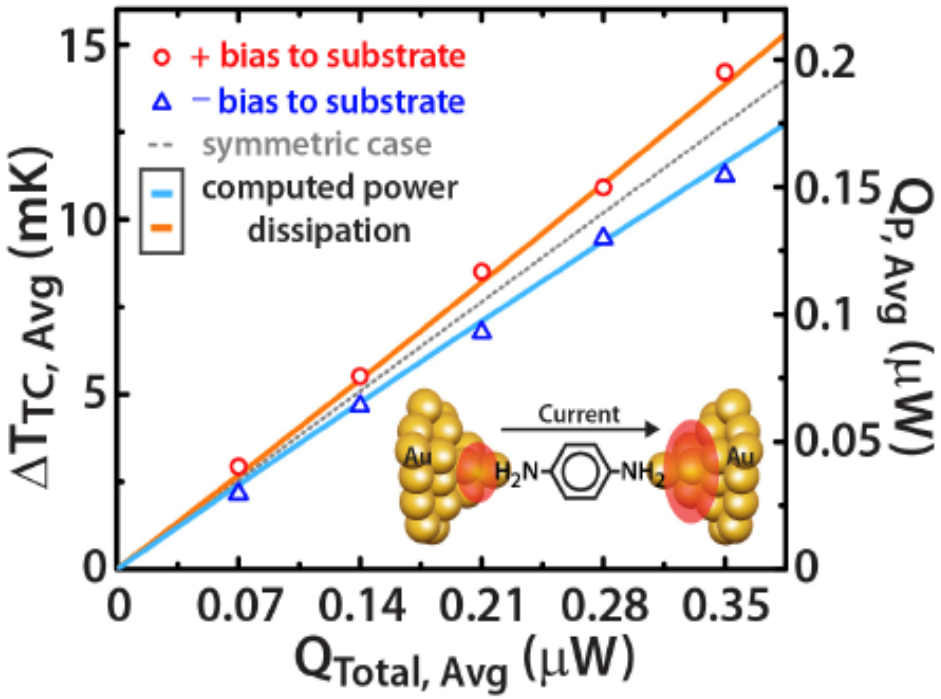
W. Lee et al., Nature 498, 209 (2013)

Benzenediamine (BDA) single-molecule junctions: Comparison between theory and experiment

DFT + NEGF



Power Dissipation



NH_2-anchors lead to hole conduction

→ Power dissipation higher for positive bias

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

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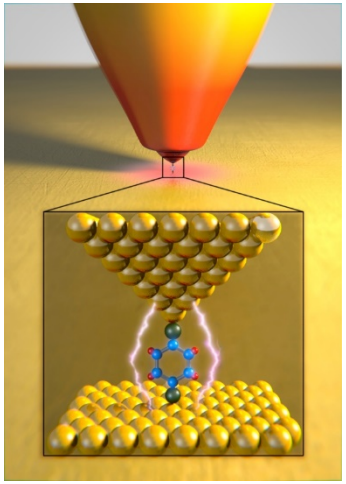


Summary – Electron and phonon transport

Electrical current

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

Fermi functions

Heat current from electrons

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

Heat current from phonons

$$I_Q^{ph} = \frac{1}{h}\int dE\, E\tau_{ph}(E)\left[n_L(E) - n_R(E)\right]$$

Bose functions

Electrical conductance

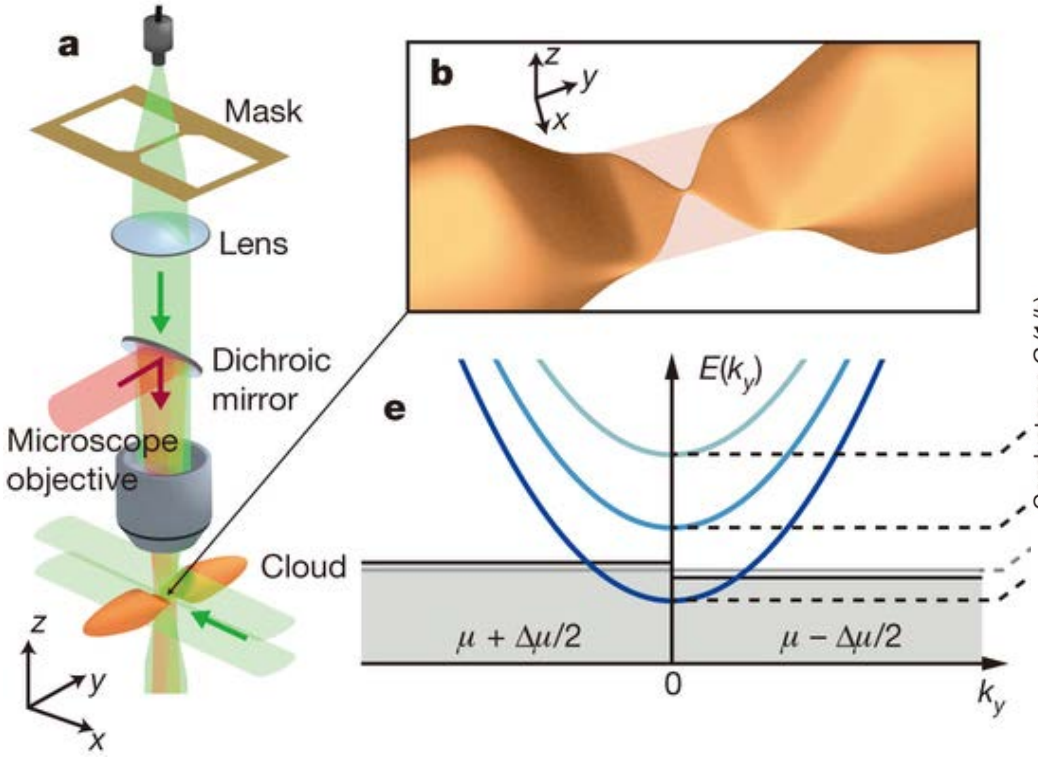
$$G = \frac{2e^2}{h}\int dE\tau(E)\left(-\frac{\partial f}{\partial E}\right)$$

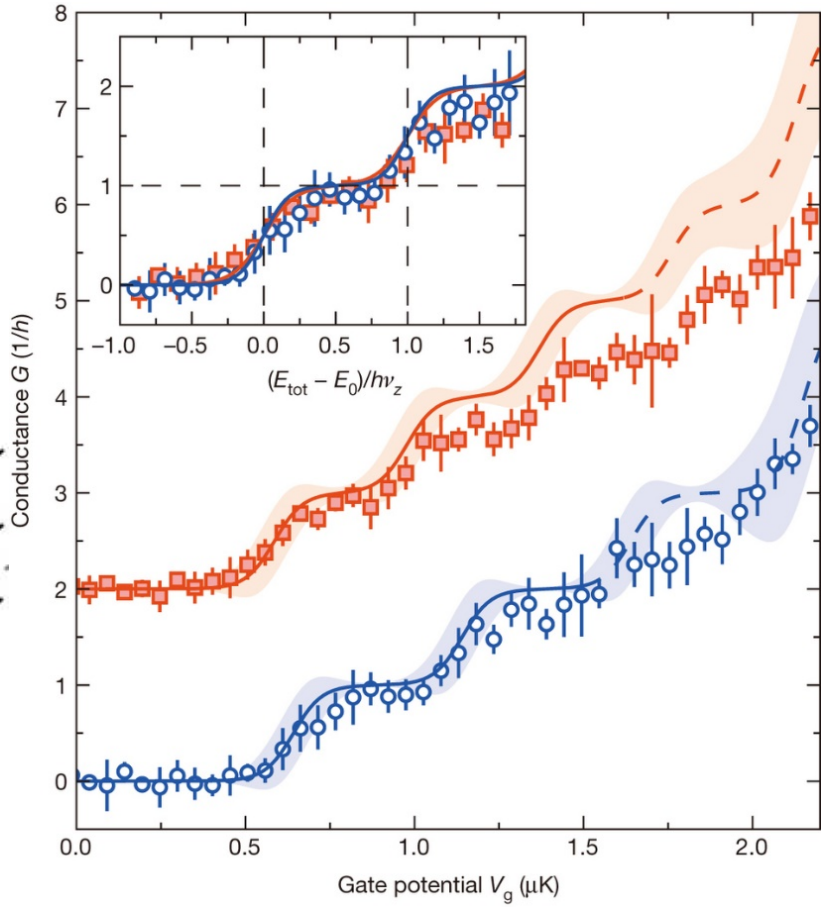
Thermal conductance

$$\kappa_{ph} = \frac{\pi^2 k_B^2 T}{3\hbar}\int dE\tau_{ph}(E)\left[\frac{3}{\pi^2}\left(\frac{E}{k_B T}\right)^2\left(-\frac{\partial n}{\partial E}\right)\right]$$

Observation of quantized conductance in neutral fermionic matter

S. Krinner, D. Stadler, D. Husmann, J.-P. Brantut , and T. Esslinger, Nature 517, 64 (2015)





Particle current (fermionic ^{6}Li atoms)

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

Thanks to …

… my group, …

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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, …