2371-18

**Advanced Workshop on Energy Transport in Low-Dimensional Systems:
Achievements and Mysteries**

15 - 24 October 2012

**Quantum Energy Transport in Electronic Nano- and Molecular Junctions
Part II**

Yonatan DUBI

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Israel*

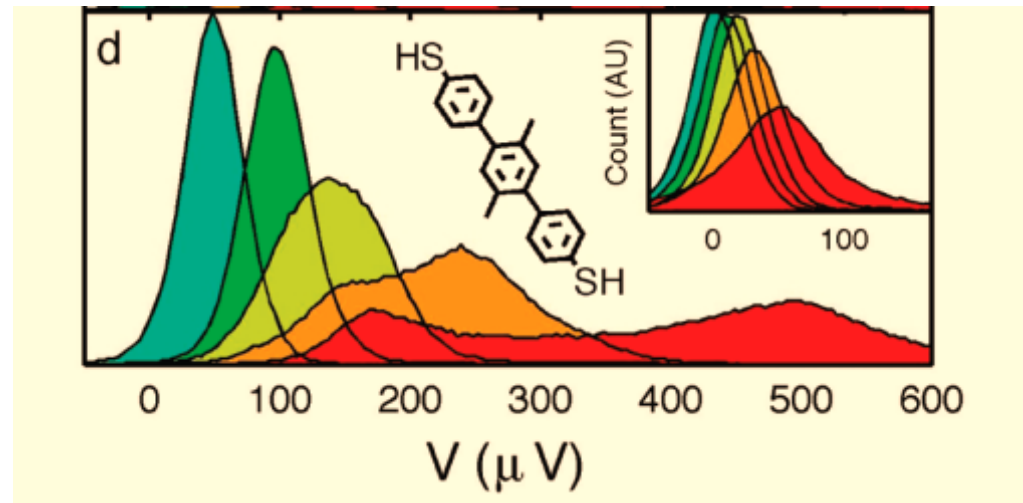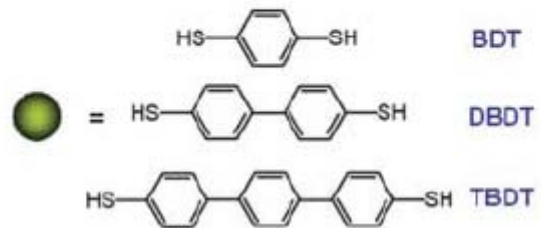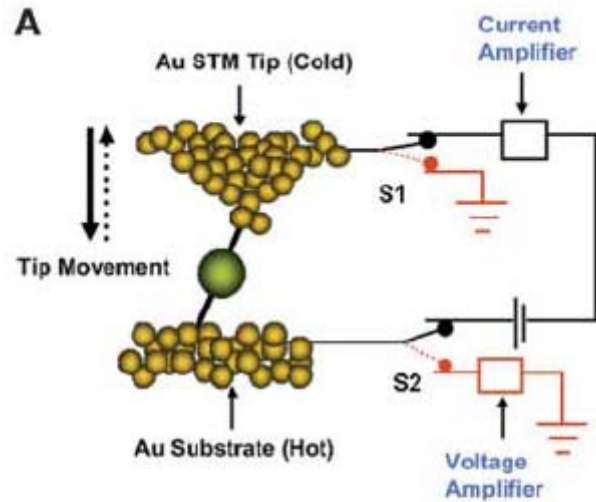# Energy transport in **electronic** nano- and molecular junctions

Yonatan Dubi

Ben-Gurion University of the Negev

ISRAEL

A

Au STM Tip (Cold)

Tip Movement

Au Substrate (Hot)

Current Amplifier

S1

S2

Voltage Amplifier

HS—◯—SH BDT

🟢 = HS—◯—◯—SH DBDT

HS—◯—◯—◯—SH TBDT

d

HS—◯—◯—◯—SH

Count (AU)

V (μV)

| ΔT≈0K | ΔT≈5K | ΔT≈10K |
| ΔT≈16K | ΔT≈20K | ΔT≈28K |

$$S_1 \approx 4.5 \frac{\mu V}{K}$$

$$S_2 \approx 15 \frac{\mu V}{K}$$

Part II.2

Theoretical description of energy transport in electronic molecular junctions:

From Green's functions to Landauer formalism

i.   Short premier to Green's functions

ii.   Meir-Wingreen formulation of transport and the Landauer formula

iii.   conductance, thermopower and thermal conductivity

iv.   selected examples

v.   The open problem of TE fluctuations

i.   Short premier to Green's functions

Note: we are talking about Fermions

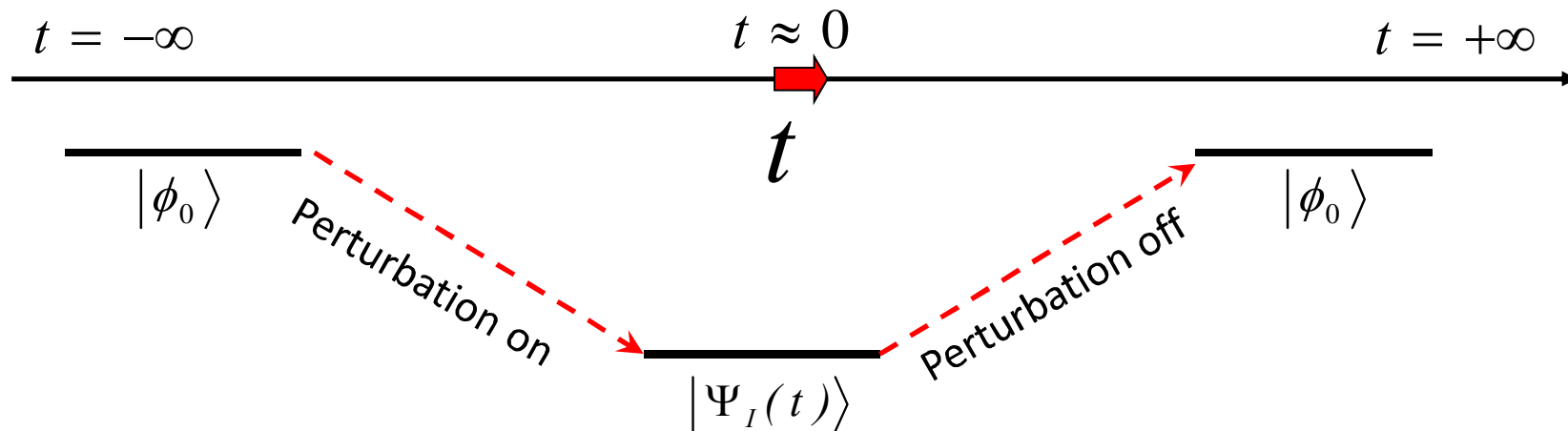(things with Bosons are slightly different, not by much)

Two "intuitive" Green's functions:

$$G^{>}(x_1, t_1; x_2, t_2) = -i\langle \psi(x_1, t_1)\psi^{\dagger}(x_2, t_2)\rangle$$

$$G^{<}(x_1, t_1; x_2, t_2) = -i\langle \psi^{\dagger}(x_2, t_2)\psi(x_1, t_1)\rangle$$

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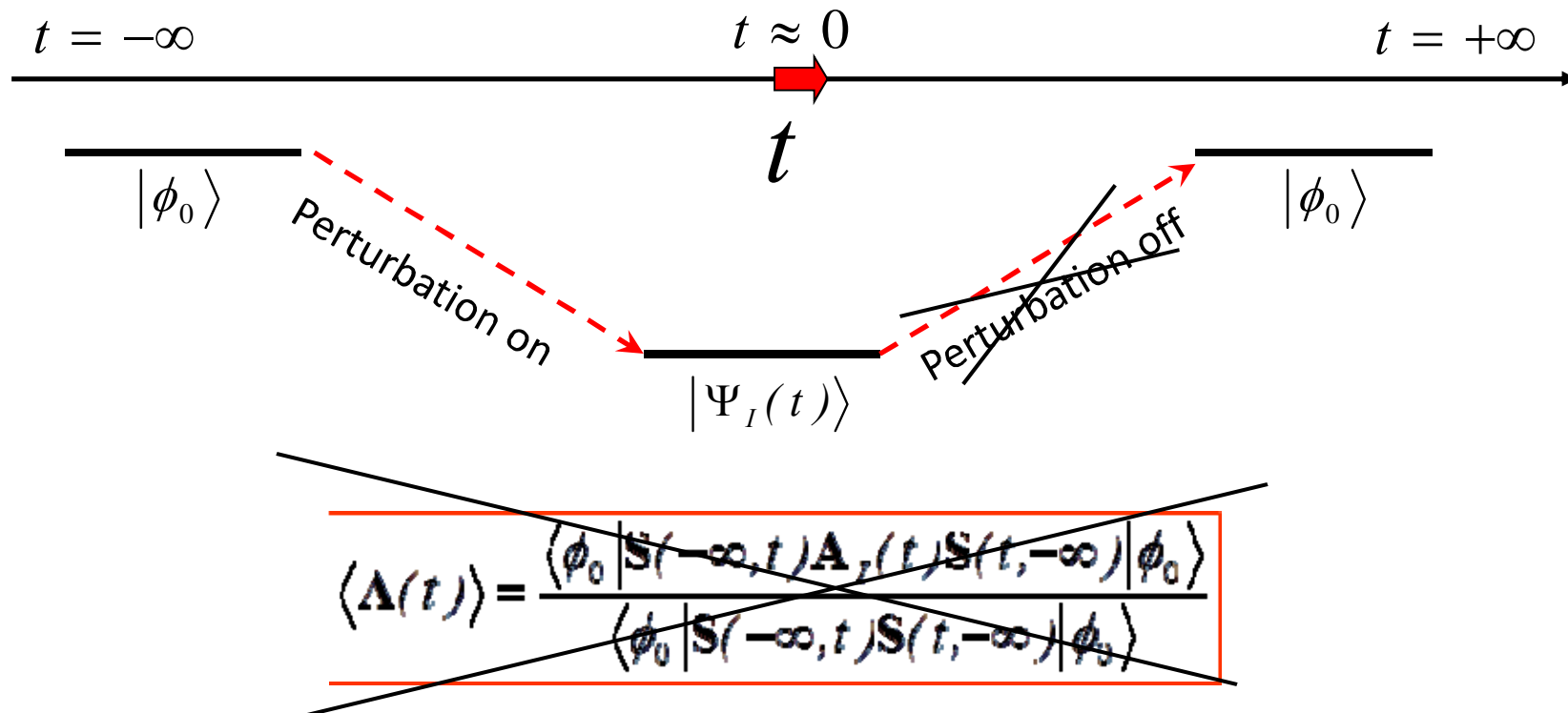Part II, 2
5

Lets remember the retarded Green's function formalism

(aim: calculate correlation functions at *T*=0 with a perturbation)
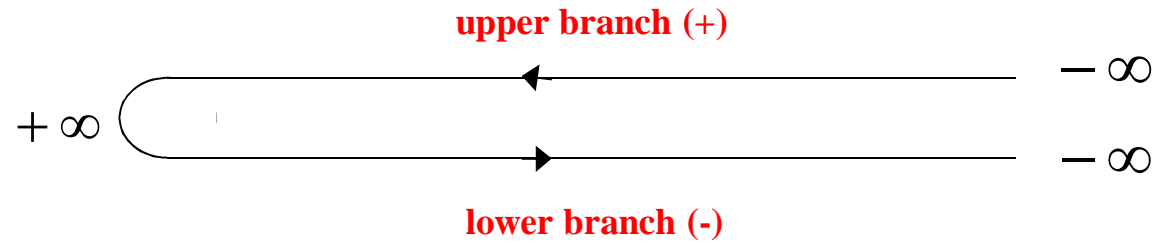

$$\langle \mathbf{A}(t) \rangle = \frac{\langle \phi_0 | \mathbf{S}(-\infty, t) \mathbf{A}_I(t) \mathbf{S}(t, -\infty) | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}(-\infty, t) \mathbf{S}(t, -\infty) | \phi_0 \rangle}$$

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6

Unfortunately, out of equilibrium – the time symmetry I broken!

$$t = -\infty \qquad\qquad t \approx 0 \qquad\qquad t = +\infty$$

$|\phi_0\rangle$

Perturbation on

$|\Psi_I(t)\rangle$

Perturbation off

$|\phi_0\rangle$

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

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7

Keldysh's formal solution: a branched time-contour

upper branch (+)

$+\infty$ $-\infty$

$-\infty$

lower branch (-)

$$G_{ij}(t_\alpha, t'_\beta) = -i \frac{\left\langle \Psi_H \left| \mathbf{T_c}\left[\mathbf{c}_{i\sigma}(t_\alpha)\mathbf{c}^+_{j\sigma}(t'_\beta)\right]\right\| \Psi_H \right\rangle}{\left\langle \Psi_H \| \Psi_H \right\rangle}, \quad \alpha, \beta = +,-$$

$$G^c_{ij}(t,t') \rightarrow \begin{pmatrix} G^{++}_{ij}(t,t') & G^<_{ij}(t,t') \\ G^>_{ij}(t,t') & G^{--}_{ij}(t,t') \end{pmatrix} \longrightarrow \textit{\textbf{Keldish 2x2 space}}$$

equilibrium

Keldish

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8

Relation between different Green's functions:

$$G^r = G^{+,+} - G^< = -G^{-,-} + G^>$$

$$G^a = G^{+,+} - G^> = -G^{-,-} + G^<$$

This makes possible to eliminate $G^{+,+}, G^{-,-}$

and work only with $G^a, G^r, G^<$

For free electrons:

$$g_k^{r,a}(\omega) = \frac{1}{\omega - E(k) \mp i\eta} \ , \ \ g_k^<(\omega) = 2\pi i f_k(\omega)\delta(\omega - E(k))$$

$$n_k = \langle c_k^\dagger c_k \rangle = \langle c_k^\dagger(0) c_k(0) \rangle = \frac{1}{2\pi i} \int d\omega \, g_k^<(\omega)$$

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Part II, 2
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9

Relation between different Green's functions:

$$G^r = G^{+,+} - G^< = -G^{-,-} + G^>$$

$$G^a = G^{+,+} - G^> = -G^{-,-} + G^<$$

Dyson equations in the presence of interactions:

$$G^< = \left(I + G^r \Sigma^r\right)g^<\left(I + \Sigma^a G^a\right) + G^r \Sigma^< G^a$$

So what does this have to do with transport ?

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \mathcal{H}_M + \mathcal{H}_{L-M} + \mathcal{H}_{R-M}$$

$$\mathcal{H}_L = \sum_k E_k \, c_{k,L}^\dagger c_{k,L}$$

$$\mathcal{H}_R = \sum_k E_k \, c_{k,R}^\dagger c_{k,R}$$

$$\mathcal{H}_M = \sum_n E_n \, d_n^\dagger d_n + \mathcal{H}_{int}$$

$$\mathcal{H}_{X-M} = \sum_k V_{k,n}^{(X)} \, c_{k,X}^\dagger d_n$$
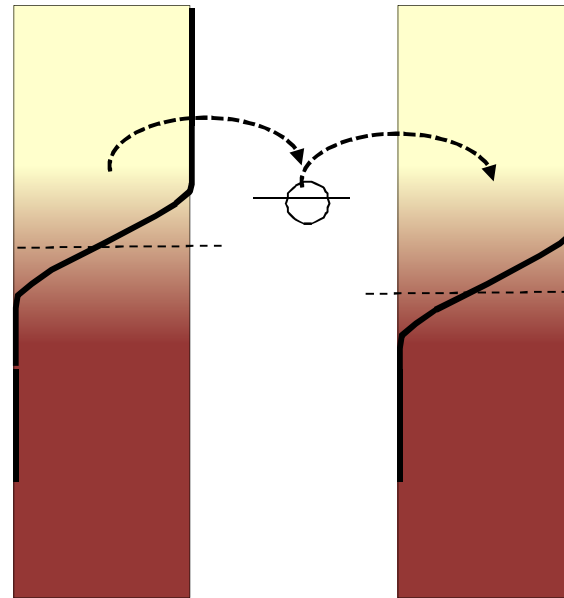
Landauer Formula for the Current through an Interacting Electron Region

Yigal Meir

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
and Department of Physics, University of California, Santa Barbara, California 93106

Ned S. Wingreen[a]

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 21 January 1992)

$$J_L = \langle \dot{n}_L \rangle = -i[\mathcal{H}, n_L]$$

$$J = \frac{ie}{\hbar} \sum_{\substack{k,a \in L \\ n}} (V_{ka,n} \langle \mathbf{c}_{ka}^\dagger \mathbf{d}_n \rangle - V_{ka,n}^* \langle \mathbf{d}_n^\dagger \mathbf{c}_{ka} \rangle)$$

$$= \frac{e}{\hbar} \sum_{\substack{k,a \in L \\ n}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} [V_{ka,n} G_{n,ka}^<(\omega) - V_{ka,n}^* G_{ka,n}^<(\omega)]$$
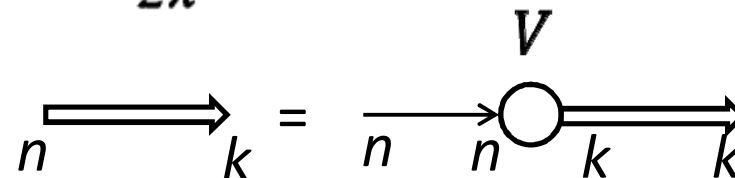
$$J = \frac{ie}{2h} \int d\epsilon (\text{tr}\{[f_L(\epsilon)\Gamma^L - f_R(\epsilon)\Gamma^R](G^r - G^a)\}$$

$$+ \text{tr}\{(\Gamma^L - \Gamma^R)G^<\}),$$

$$\text{where} \quad \Gamma_{n,m}^L = 2\pi \sum_{a \in L} \rho_a(\epsilon) V_{a,n}(\epsilon) V_{a,m}^*(\epsilon)$$

And if the coupling to the electrodes is (essentially) symmetric then:

$$J = \frac{ie}{h} \int d\epsilon [f_L(\epsilon) \text{-} f_R(\epsilon)] \, \text{Tr}\{\boldsymbol{\Gamma}(\boldsymbol{G}^r - \boldsymbol{G}^a)\}$$

And for the non-interacting system

$$J = \frac{ie}{h} \int d\epsilon [f_L(\epsilon) \text{-} f_R(\epsilon)] \, \text{Tr}\{\boldsymbol{G}^a \boldsymbol{\Gamma}^R \boldsymbol{G}^r \boldsymbol{\Gamma}^L\} = \int d\epsilon \left[f_L(\epsilon) \text{-} f_R(\epsilon) \right] T(\epsilon)$$

Similarly

$$J_Q = \int d\epsilon [f_L(\epsilon) \text{-} f_R(\epsilon)](\epsilon - \mu) T(\epsilon)$$

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Part II, 2

13

$$\begin{pmatrix} J \\ J_Q \end{pmatrix} = \begin{pmatrix} G & GS \\ GS & (GS^2 + \kappa) \end{pmatrix} \begin{pmatrix} \Delta V \\ \Delta T \end{pmatrix}$$

So by setting $\mu_{L(R)} = \mu \pm \frac{e\Delta V}{2}, \quad T_{L(R)} = T \pm \frac{\Delta T}{2}$

One immediately finds

$$G = \frac{J}{\Delta V}\Big|_{\Delta T=0} = e^2 L_0$$

$$S = \frac{\Delta V}{\Delta T}\Big|_{J=0} = L_1/(eTL_0)$$

$$\kappa_e = \frac{J_Q}{\Delta T}\Big|_{J=0} = (L_2 - \frac{L_1^2}{L_0})/T$$

With

$$L_n = \frac{1}{h} \int d\epsilon\, T(\epsilon)(\epsilon - \mu)^2 (-\frac{\partial f}{\partial \epsilon})$$

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14

Low-temperature limit:

$$G = \frac{2e^2}{h} T(\epsilon) \Big|_{\epsilon=\mu}$$

$$S = -\frac{\pi^2 k_B^2 T}{3e} \frac{\partial \log T(E)}{\partial E} \Big|_{\epsilon=\mu}$$

Key publications:

Thermoelectric effect in molecular electronics

Magnus Paulsson* and Supriyo Datta[†]
*Purdue University, School Of Electrical & Computer Engineering, 1285 Electrical Engineering Building,
West Lafayette, Indiana 47907-1285, USA*

Thermoelectric effect in molecular junctions: A tool for revealing transport mechanisms

Dvira Segal
Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel

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Part II-2
15

Conductance and transmission for the single-resonant level

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \mathcal{H}_M + \mathcal{H}_{L-M} + \mathcal{H}_{R-M}$$

$$\mathcal{H}_L = \sum_k E_k\, c_{k,L}^\dagger c_{k,L} \quad \mathcal{H}_R = \sum_k E_k\, c_{k,R}^\dagger c_{k,R} \quad \mathcal{H}_M = \sum_n E_n\, d_n^\dagger$$

$$\mathcal{H}_{X-M} = \sum_k V_{k,n}^{(X)}\, c_{k,X}^\dagger d_n$$

$$\Sigma = \Sigma_L + \Sigma_R, \;\; \Sigma_X = -i\Gamma_X = -i\sum_k \rho_k V_{k,n}^{(X)}$$

Since the molecule is non-interacting:

$$G_n^r(\omega) = g_n^r(\omega) + g_n^r(\omega)\Sigma G_n^r(\omega)$$

or

$$G_n^r(\omega) = ([g_n^r(\omega)]^{-1} + \Sigma)^{-1} = \frac{1}{\omega - E_n - i\Gamma}$$

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Part II, 2
dimensional systems Oct. 2012
16

$$G_n^r(\omega) = \frac{1}{\omega - E_n - i\Gamma} \qquad G_n^a(\omega) = \frac{1}{\omega - E_n + i\Gamma}$$

$$J = \frac{ie}{h} \int d\epsilon [f_L(\epsilon) - f_R(\epsilon)] \, \mathrm{Tr}\{G^a \Gamma^R G^r \Gamma^L\}$$

$$J = \frac{2e}{h} \int d\epsilon [f_L(\epsilon) - f_R(\epsilon)] \sum_n \frac{\Gamma_n^2}{(\omega - E_n)^2 + \Gamma_n^2}$$

Or $\quad G = \dfrac{2e^2}{h} \sum_n \dfrac{\Gamma_n^2}{(E_F - E_n)^2 + \Gamma_n^2}$

$$S = -\frac{\pi^2 k_B^2 T}{3e} \sum_n \frac{(E_F - E_n)}{(\omega - E_n)^2 + \Gamma_n^2}$$
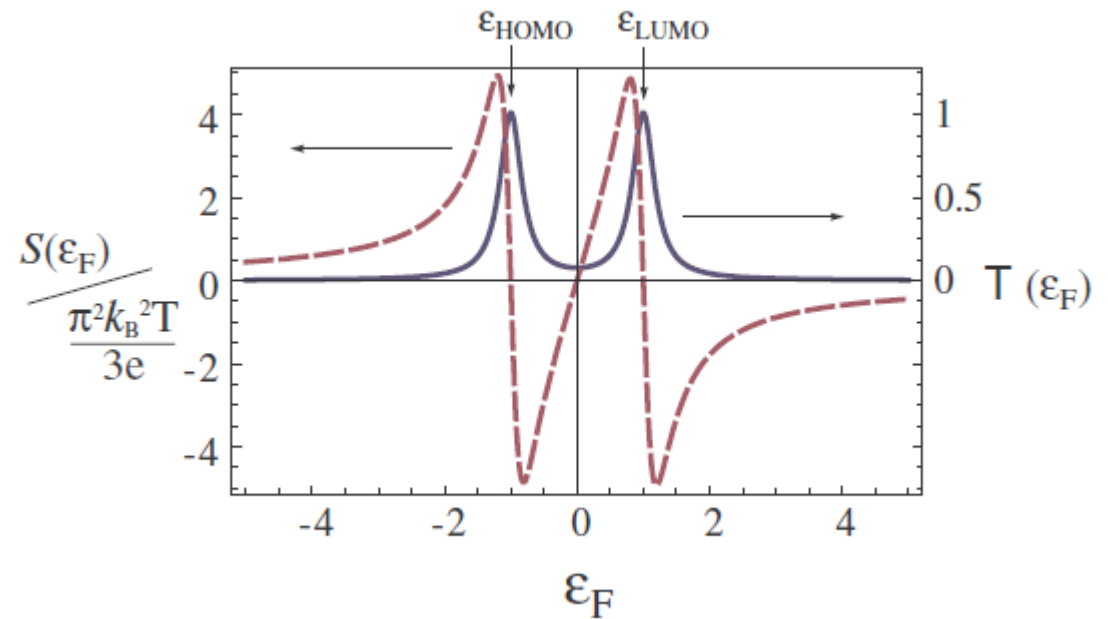
Optimal thermoelectric figure of merit of a molecular junction

Padraig Murphy,[1] Subroto Mukerjee,[1,2] and Joel Moore[1,2]

$$I = -\frac{e}{h}\int_{-2t}^{2t} dE[\mathcal{T}_\uparrow(E) + \mathcal{T}_\downarrow(E)][f_L^0(E) - f_R^0(E)],$$

$$\mathcal{T}_\sigma(E) = \frac{\Gamma_L\Gamma_R}{\bar{\Gamma}}\frac{\bar{\Gamma}}{\bar{\Gamma}^2 + (E - \varepsilon_d)^2}.$$

$$I_Q^{\text{el}} = \frac{1}{h}\int_{-2t}^{2t} dE(E - \mu)[\mathcal{T}_\uparrow(E) + \mathcal{T}_\downarrow(E)][f_L^0(E) - f_R^0(E)].$$

$$\gamma_{L(R)} = \Gamma_{L(R)}/(k_BT), \quad \bar{\gamma} = \bar{\Gamma}/(k_BT), \quad \delta = (\varepsilon_d - \mu)/(k_BT),$$

$$I = -\frac{2e}{h}\frac{\gamma_L\gamma_R}{\bar{\gamma}}[\mathcal{F}_0(\bar{\gamma}, \delta)eV + \mathcal{F}_1(\bar{\gamma}, \delta)k_B\Delta T],$$

$$I_Q^{\text{el}} = \frac{2k_BT}{h}\frac{\gamma_L\gamma_R}{\bar{\gamma}}[\mathcal{F}_1(\bar{\gamma}, \delta)eV + \mathcal{F}_2(\bar{\gamma}, \delta)k_B\Delta T],$$

$$ZT = \frac{1}{\bar{\gamma}}\frac{\pi\delta^2}{4\cosh^2(\delta/2)} + \mathcal{O}(\bar{\gamma}^0)$$
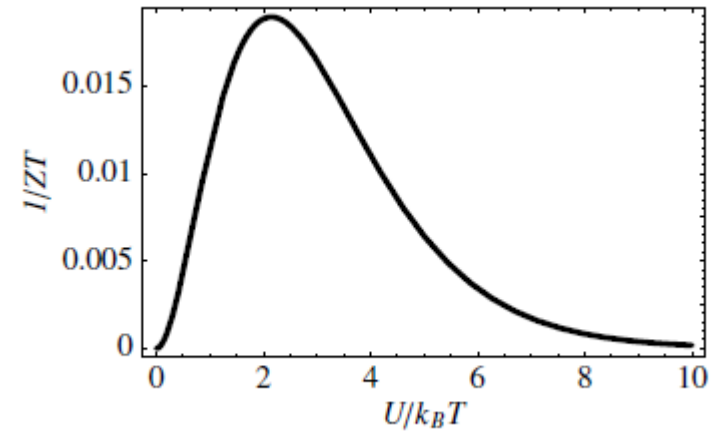
Microwave-mediated heat transport in a quantum dot attached to leads

Feng Chi[1] and Yonatan Dubi[2,3]

[1] College of Engineering, Bohai University, Jinzhou 121013, People's Republic of China
[2] Sackler School of Physics and Astronomy, Tel Aviv University, Tel Aviv 69978, Israel
[3] Landa Laboratories, 3 Pekeris Street, Rehovot 76702, Israel

$$H(t) = \sum_{k,\sigma,\beta} \varepsilon_{k\beta}(t) c_{k\beta\sigma}^{\dagger} c_{k\beta\sigma} + \sum_{\sigma} \varepsilon_d(t) d_\sigma^{\dagger} d_\sigma +$$
$$+ U d_\uparrow^{\dagger} d_\uparrow d_\downarrow^{\dagger} d_\downarrow + \sum_{k,\sigma,\beta} (V_{\beta d} c_{k\beta\sigma}^{\dagger} d_\sigma + \text{H.c.}), \quad (1)$$
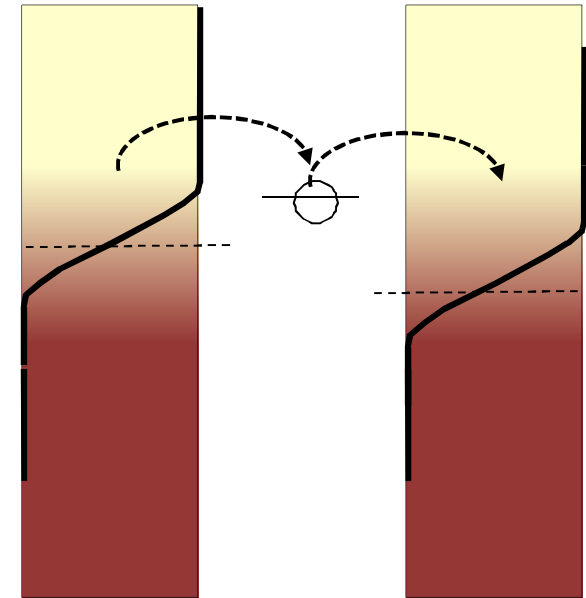
$$H(t) = \sum_{k,\sigma,\beta} \varepsilon_{k\beta}(t)c_{k\beta\sigma}^{\dagger}c_{k\beta\sigma} + \sum_{\sigma} \varepsilon_{d}(t)d_{\sigma}^{\dagger}d_{\sigma} + Ud_{\uparrow}^{\dagger}d_{\uparrow}d_{\downarrow}^{\dagger}d_{\downarrow} + \sum_{k,\sigma,\beta} (V_{\beta d}c_{k\beta\sigma}^{\dagger}d_{\sigma} + \text{H.c.}),$$

$$\begin{pmatrix} J \\ Q \end{pmatrix} = \frac{2}{h}\frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R}\sum_{\sigma}\int d\varepsilon \begin{pmatrix} -e \\ \varepsilon - E_F \end{pmatrix} \times [f_L(\varepsilon)\text{Im}\langle A_{L\sigma}(\varepsilon,t)\rangle - f_R(\varepsilon)\text{Im}\langle A_{R\sigma}(\varepsilon,t)\rangle],$$

$$A_{\beta\sigma}(\varepsilon,t) = \int_{-\infty}^{t} dt_1 G_{\sigma}^{r}(t,t_1)\exp\left[-\mathrm{i}\varepsilon(t_1 - t) - \mathrm{i}\int_{t}^{t_1}\Delta_{\beta}(\tau)\,d\tau\right],$$

$$G_{\sigma}^{r}(t,t') = -\mathrm{i}\theta(t - t')\left\{(1 - n_{\bar{\sigma}})\right.$$

$$\times \exp\left(-\mathrm{i}\int_{t'}^{t}\varepsilon_{d}(\tau)\,d\tau - \frac{\Gamma}{2}(1 - n_{\bar{\sigma}})(t - t')\right)$$

$$\left. + n_{\bar{\sigma}}\exp\left(-\mathrm{i}\int_{t'}^{t}[\varepsilon_{d}(\tau) + U]\,d\tau - \frac{\Gamma}{2}n_{\bar{\sigma}}(t - t')\right)\right\}$$

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Part II, 2

20

$$A_{\beta\sigma}(\varepsilon,t) = \sum_{k,k'} J_k(\frac{\Delta_d - \Delta_\beta}{\omega}) J_{k'}(\frac{\Delta_\beta - \Delta_d}{\omega}) e^{i(k+k')\omega t}$$

$$\times \{\frac{1 - n_{\bar\sigma}}{\varepsilon - \varepsilon_d - k'\omega + i\Gamma(1-n_{\bar\sigma})/2} + \frac{n_{\bar\sigma}}{\varepsilon - \varepsilon_d - U - k'\omega + i\Gamma n_{\bar\sigma}/2}\}$$

$$= \sum_k J_k^2(\frac{\Delta_d - \Delta_\beta}{\omega})[\frac{1 - n_{\bar\sigma}}{\varepsilon - \varepsilon_d - k\omega + i\Gamma(1-n_{\bar\sigma})/2} + \frac{n_{\bar\sigma}}{\varepsilon - \varepsilon_d - U - k\omega + i\Gamma n_{\bar\sigma}/2}].$$
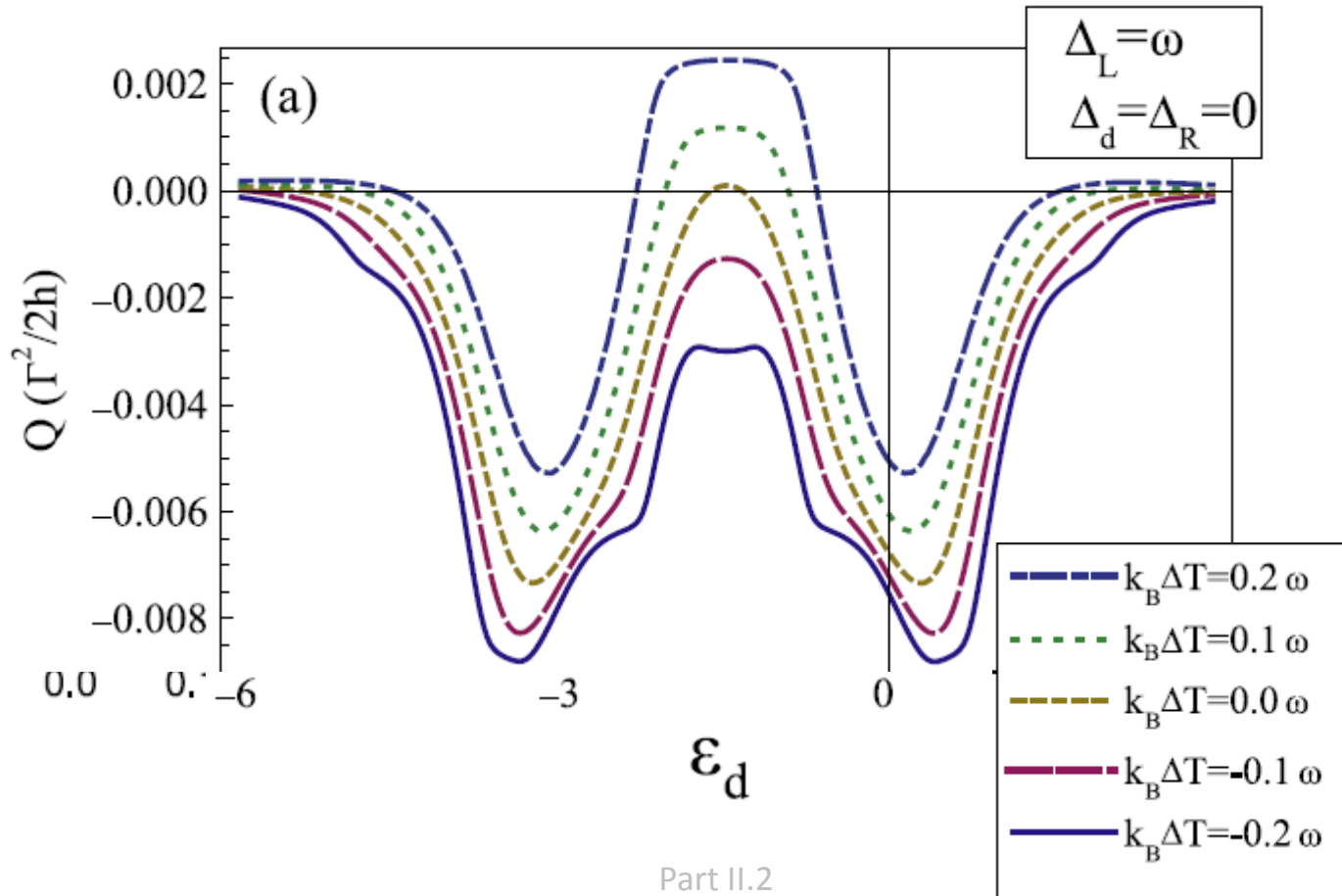
NEGF+DFT

- Use DFT to calculate the Green's functions

- Use Green's function to calculate *T(E)* via Landauer formula *Use*

- *T(E)* to calculate thermopower
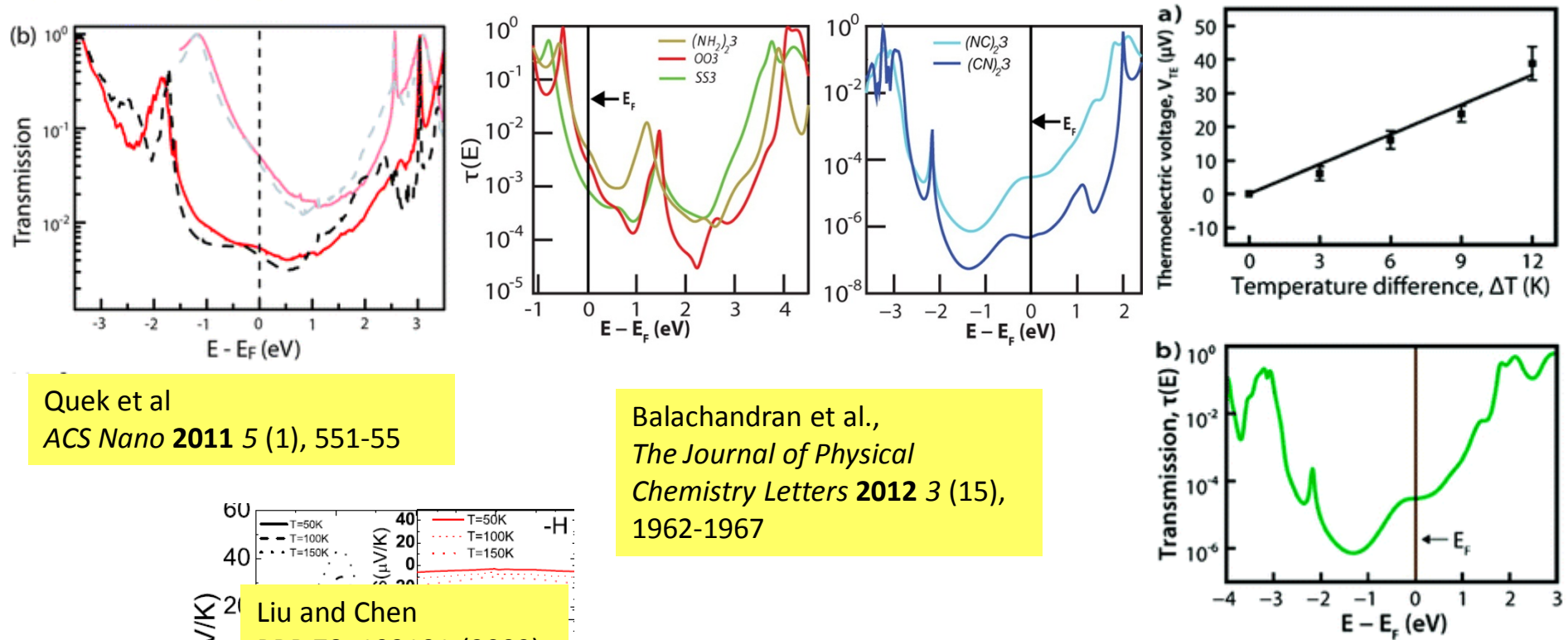
Quek et al
ACS Nano **2011** *5* (1), 551-55

Balachandran et al.,
The Journal of Physical Chemistry Letters **2012** *3* (15), 1962-1967
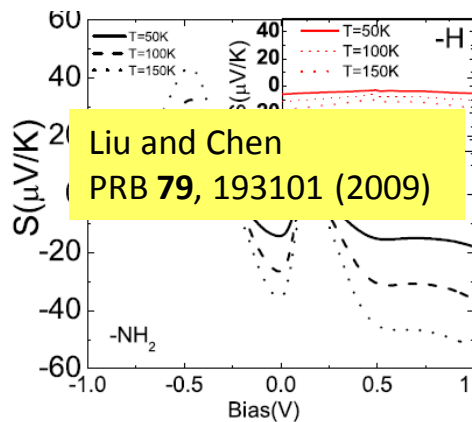
Liu and Chen
PRB **79**, 193101 (2009)

Tan et al.,
Journal of the American Chemical Society **2011** *133* (23), 8838-8841

Does this: # Explain this:

16 MARCH 2007 VOL 315 **SCIENCE** www.sciencemag.org
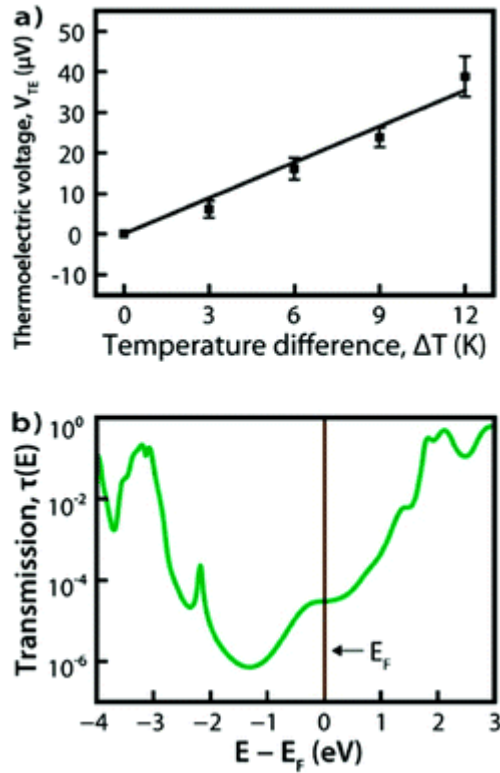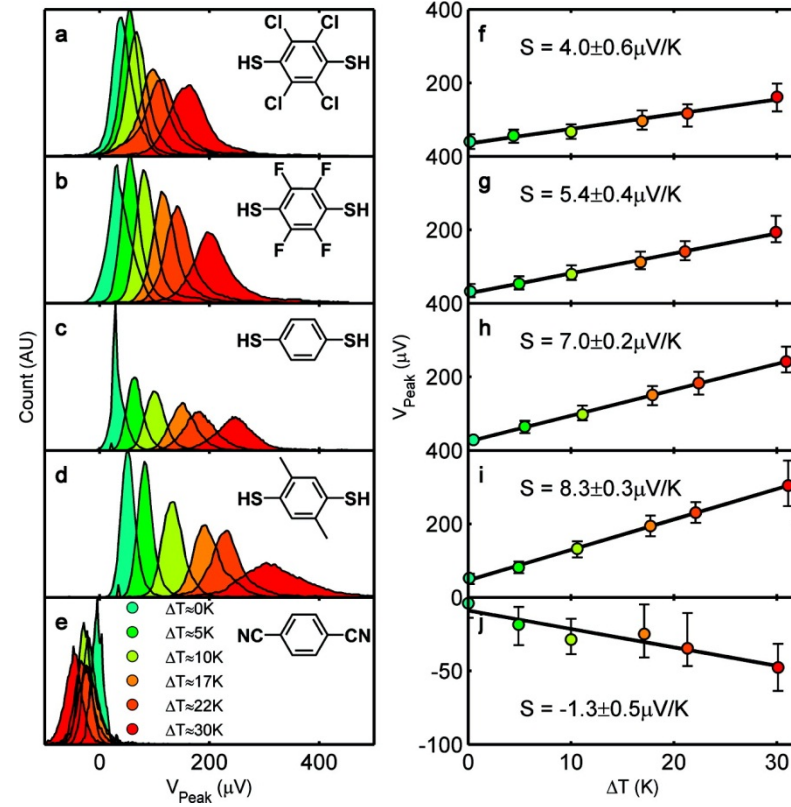
Thermoelectricity in Molecular Junctions

Pramod Reddy,[1]* Sung-Yeon Jang,[2,3]*† Rachel A. Segalman,[1,2,3]‡ Arun Majumdar[1,3,4]‡
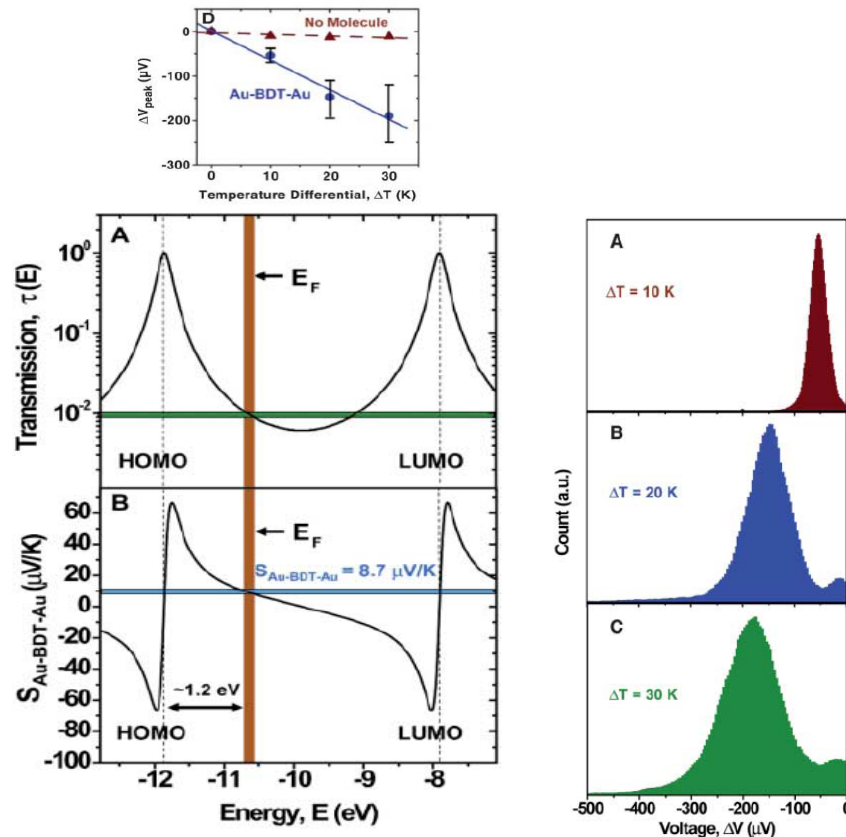
- Extremely impressive experiment !!
- Analysis based on Landauer Formula:
  - not at the low *T* limit
  - not necessarily in Linear response
  - Fluctuations not accounted for
  - Additional structure not explained

Analysis of thermopower fluctuations with Landauer:

$$S_1 \approx 4.5 \; \frac{\mu V}{K}$$

$$S_2 \approx 15 \; \frac{\mu V}{K}$$

$$G = \frac{e^2}{h} \frac{\Gamma^2}{(E_n - E_F)^2 + \Gamma^2}$$
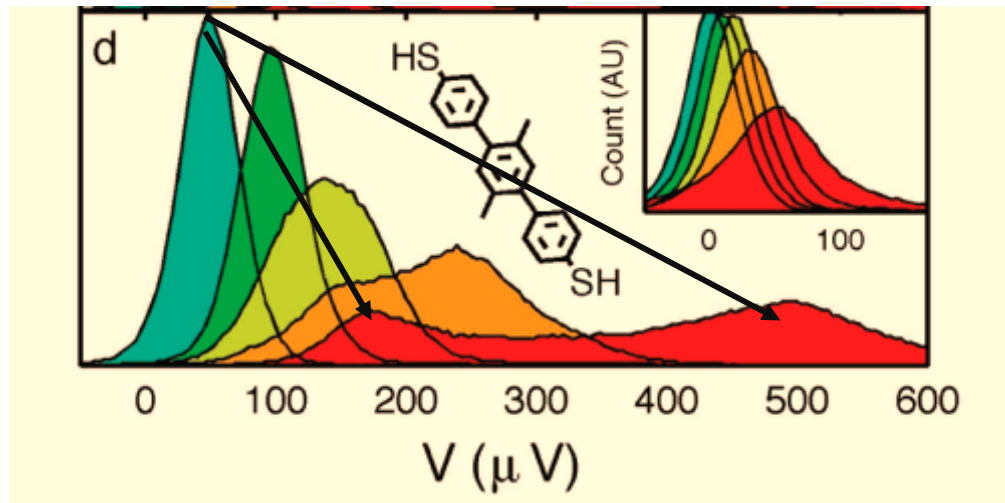
$$S = \frac{2\pi^2 k_B^2 T}{3e} \frac{(E_n - E_F)}{\Gamma^2 + (E_n - E_F)^2}$$

What should be fluctuations in E_n to give these two values of S?

$$E_n \rightarrow E_n + \delta E$$

One finds:

$$\Gamma \sim 0.3 \; eV, E_n \sim 3eV, \delta E \sim 2.2 eV, \frac{\delta E}{E} \sim 70\%$$

Analysis of thermopower fluctuations with Landauer:

$$S = \frac{2\pi^2 k_B^2 T}{3e} \frac{(E_n - E_F)}{\Gamma^2 + (E_n - E_F)^2}$$

Taking E_n to be a (Gaussian) random number, I obtain the distribution

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Part II, 2

26
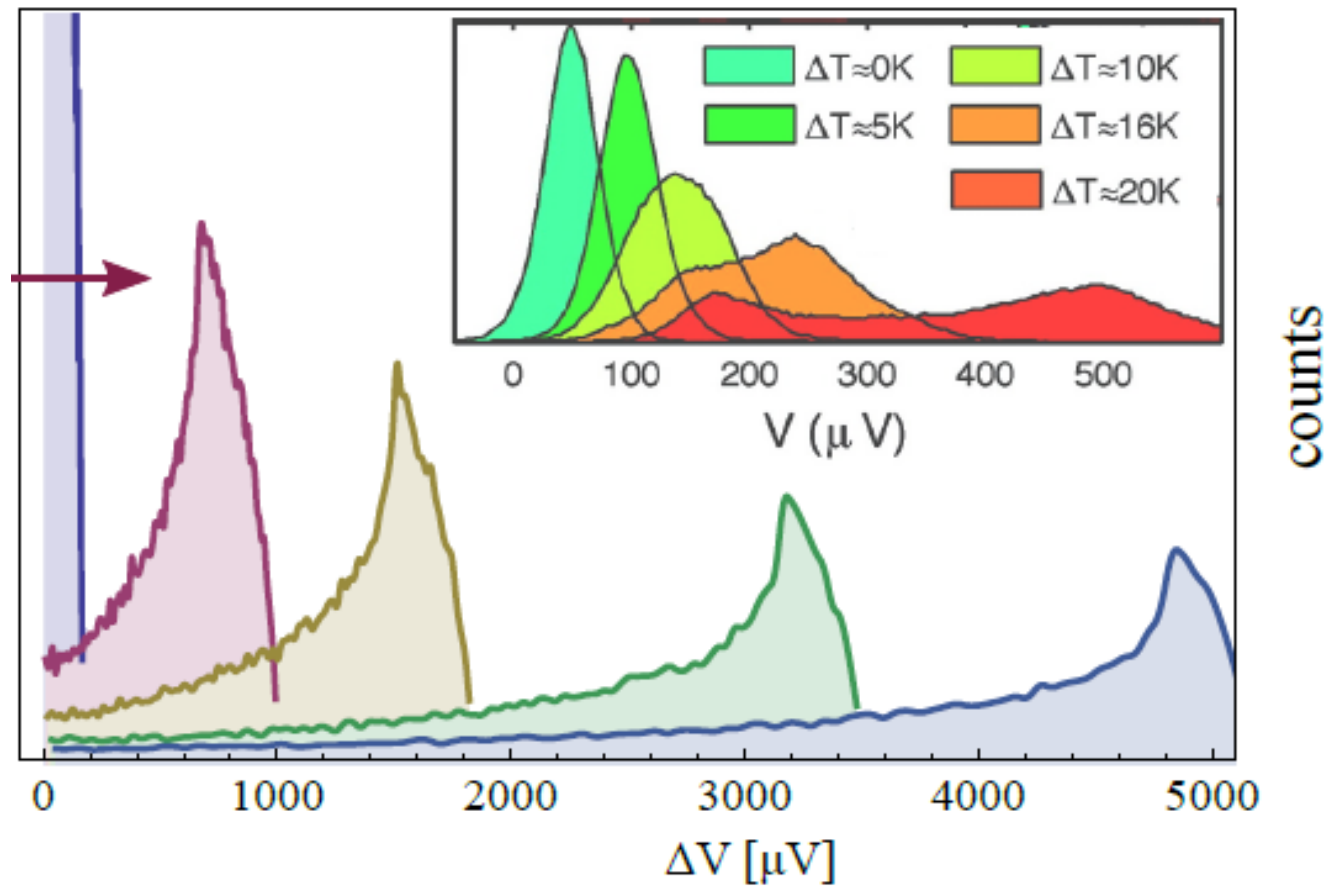
Intermediate Summary : The NEGF and the Landauer formula

- straight-forward derivation

- "Easy" to implement

- Incompatible with Density Functional Theory:

  - Use of KS orbitals to calculate transmission

  - A zero temperature calculation

  - Does not include fluctuations (of any kind)

  - fully coherent

- implies huge energy fluctuations

- post-dicts wrong thermo-voltage distribution

An open Quantum System Approach

Alternative route : Open Quantum System approach

Main Differences from NEGF:

- Finite system

- Open System (compatible with TD-DFT, non-equilibrium)

- Dynamical system (time dependent effects, interactions)

An open Quantum System Approach

Starting point – Many-Body Stochastic Schrödinger Eq.:

$$\partial_t \Psi(\mathbf{r},t) = -i\hat{H}(t)\Psi(\mathbf{r},t) - \tfrac{1}{2}\hat{V}^+\hat{V}\Psi(\mathbf{r},t) + \hat{V}\, l(t)\Psi(\mathbf{r},t)$$

Wave-function

System (geometry, interactions)

Environment (temperature(s))

[Di Ventra & D'agosta, PRL 98, 226403 (2007)]

For derivation from microscopic theory:
Gaspard & Nagaoka, *Non-Markovian stochastic Schrodinger equation*,
Journal of Chemical Physics **111** (1999) 5676-5690

An open Quantum System Approach

Starting point – Many-Body Stochastic Schrödinger Eq.:

$$\partial_t \Psi(\mathbf{r}, t) = -i\hat{H}(t)\Psi(\mathbf{r}, t) - \tfrac{1}{2}\hat{V}^+\hat{V}\Psi(\mathbf{r}, t) + \hat{V}\, l(t)\Psi(\mathbf{r}, t)$$

Wave-
function

System
(geometry,
interactions)

Environment (temperature(s))

This equation :

- Conserves norm *on average*

- Hamiltonian and *V*-operators can be interacting and time-dependent

An open Quantum System Approach

Starting point – Many-Body Stochastic Schrödinger Eq.:

$$\partial_t \Psi(\mathbf{r},t) = -i\hat{H}(t)\Psi(\mathbf{r},t) - \tfrac{1}{2}\hat{V}^+\hat{V}\Psi(\mathbf{r},t) + \hat{V}\, l(t)\Psi(\mathbf{r},t)$$

To show norm conservation (and derive the Master equation)

$$d\Psi(\mathbf{r},t) = [-(i\hat{H}(t) - \tfrac{1}{2}\hat{V}^+\hat{V})dt + \hat{V}\, l(t)dt]\Psi(\mathbf{r},t)$$

$$= [-(i\hat{H}(t) - \tfrac{1}{2}\hat{V}^+\hat{V})dt + \hat{V}\, d\mathrm{W}]\Psi(\mathbf{r},t)$$

$$\overline{dW} \sim \sqrt{dt}$$

And Ito chain rule:

$$d(\Psi\Phi) = (d\Psi)\Phi + \Psi(d\Phi) + d\Psi d\Phi$$

An open Quantum System Approach

$$d\Psi(\mathbf{r},t) = [-(i\hat{H}(t) - \tfrac{1}{2}\hat{V}^{+}\hat{V})dt + \hat{V}\,d\mathrm{W}]\Psi(\mathbf{r},t)$$

$$d(\Psi^{*}\Psi) \sim -\hat{V}^{+}\hat{V}dt + \hat{V}^{+}\hat{V}(dW\,dW')$$

and so

$$\overline{d(\Psi^{*}\Psi)} \sim -\hat{V}^{+}\hat{V}dt + \hat{V}^{+}\hat{V}\overline{(dW\,dW')} = 0$$

An open Quantum System Approach

Starting point – Many-Body Stochastic Schrödinger Eq.:

$$\partial_t \Psi(\mathbf{r},t) = -i\hat{H}(t)\Psi(\mathbf{r},t) - \tfrac{1}{2}\hat{V}^+\hat{V}\Psi(\mathbf{r},t) + \hat{V}\, l(t)\Psi(\mathbf{r},t)$$

Wave-
function

System
(geometry,
interactions)

Environment (temperature(s))

This equation :

- Conserves norm *on average*

- Hamiltonian and *V*-operators can be interacting and time-dependent

An open Quantum System Approach

New Ingredients:
$$\partial_t \Psi(\mathbf{r},t) = -i\hat{H}(t)\Psi(\mathbf{r},t) - \tfrac{1}{2}\hat{V}^{+}\hat{V}\Psi(\mathbf{r},t) + \hat{V}\,l(t)\Psi(\mathbf{r},t)$$

1. V-operators : describe the relation between environment and system

2. xc – functionals for open systems

Local relaxation from leads

T_L T_R
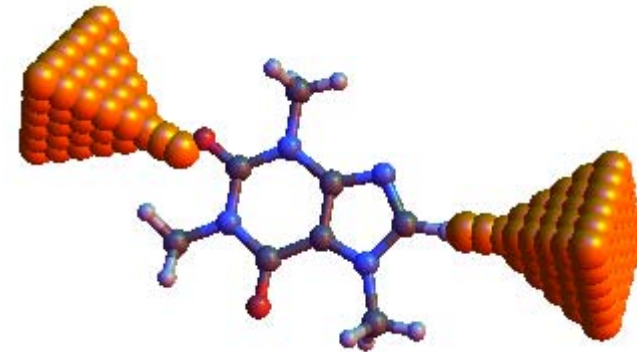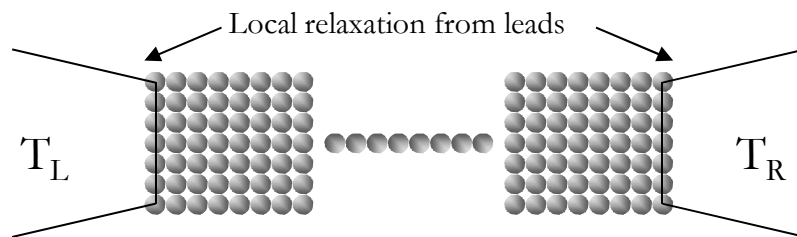
aim: find "reasonable" V-Operators to study the open system *out of equilibrium*

An open Quantum System Approach

Step 1: from the many-body wave function to the
      density matrix:

$$\hat{\rho} = \overline{\left| \Psi(t) \right\rangle \left\langle \Psi(t) \right|}$$

Hamiltonian term

Relaxation term
(environment)

$$\dot{\hat{\rho}}_{MB} = -i[\mathcal{H}, \hat{\rho}_{MB}] + \mathcal{L}\hat{\rho}_{MB}$$

$$\mathcal{L}\hat{\rho}_{MB} = \sum_i \left(V_i \hat{\rho}_{MB} V_i^+ - \tfrac{1}{2}\{V_i^+ V_i, \hat{\rho}_{MB}\} \right)$$

[Huang & Huang
Chinese J. Phys. **42** (3) 221 (2004)]

- Environment taken in the Markov approximation

[T. Prosen et. al, arXiv:1204.1321,
arXiv:1205.1167]

- Non-interacting electrons

- constant number of electrons (canonical ensemble)

- $\hat{\rho}$ is the full Many-Body density matrix – scales as $\sim e^{N_e \log N_e}$

Even without interactions – a formidable task!

An open Quantum System Approach

Step 2: from the *many-body* density matrix to a *single-particle* density matrix:

$$\rho = \sum_{kk'} \rho_{kk'} |k\rangle\langle k'| \quad , \quad \rho_{kk'} = \text{Tr}\left(c_k^+ c_k \hat{\rho}\right)$$

$$n_k = \rho_{kk} \, , \quad \text{Tr}(\rho) = N_e$$

[Pershin, Dubi & Di Ventra,
PRB **78**, 054302 (2008)]

Ansatz : $\quad \langle A \rangle = \text{Tr}\left(A \hat{\rho}_{MB}\right) = \sum_i \text{Tr}\left(A \rho^{(i)}\right)$

Need to be
determined

$$\hat{\rho}^{(i)} = -i[\mathcal{H}, \hat{\rho}^{(i)}] + \mathcal{L}^{(i)} \hat{\rho}^{(i)}$$

$$\mathcal{L}^{(i)} \hat{\rho}^{(i)} = \sum_{k \neq k'} \left(V_{kk'}^{(i)} \hat{\rho}^{(i)} (V_{kk'}^{(i)})^+ - \tfrac{1}{2}\{(V_{kk'}^{(i)})^+ V_{kk'}^{(i)}, \hat{\rho}^{(i)}\}\right)$$

We have : **An effective single particle (matrix) equation**

We need to :

Solve a set of matrix equation – The matrix size scales as ~N **!**

36

An open Quantum System Approach

$$\dot{\hat{\rho}} = -i[\mathcal{H}, \hat{\rho}] + \mathcal{L}\rho$$

Wave-function

System (geometry, interactions)

Environment

$$\hat{\rho}_{kk'} = \mathrm{Tr}(c_k^+ c_k \rho_M)$$

$$\mathcal{L}\hat{\rho} = -\tfrac{1}{2}\{V^+ V, \hat{\rho}\} + V\rho V^+$$

$$V_{kk'}^{(\mathrm{L,R})} = \sqrt{\gamma_{kk'} f_D(\varepsilon_k)} |k\rangle\langle k'|$$

$$f_D(\varepsilon_k) = \frac{1}{\exp\left(\dfrac{\varepsilon_k - \mu}{T}\right) + 1}$$

*Reminder: this is also the strategy for DFT

** but in DFT – only ground-state

An open Quantum System Approach

Comparison between full Many-Body and Single-Particle equations:

Example 1 – driven system at T=0

$$\mathcal{H} = -t\sum_i \left(e^{2\pi i\phi/\phi_0} c_i^+ c_{i+1} + h.c.\right) + \sum_i V_i(t)\, c_i^+ c_i$$

$$\mathbf{E} = E_0(\mathbf{x}\cos(\omega t) + \mathbf{y}\sin(\omega t))$$

$$V_{kk'}^{(i)} = \sqrt{\gamma\, f_D(\varepsilon_k)}\,\delta_{ik}\,(1-\delta_{kk'})|k\rangle\langle k'|$$
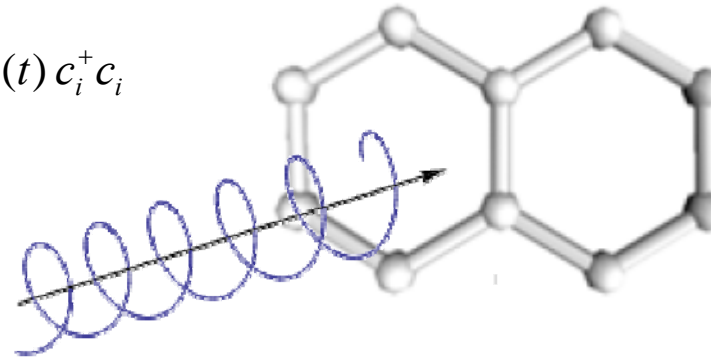
$$J = \tfrac{ie}{\hbar}\left\langle c_i^+ c_{i+1} - h.c.\right\rangle$$
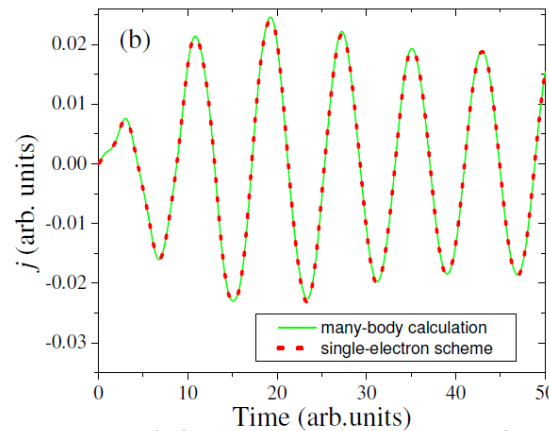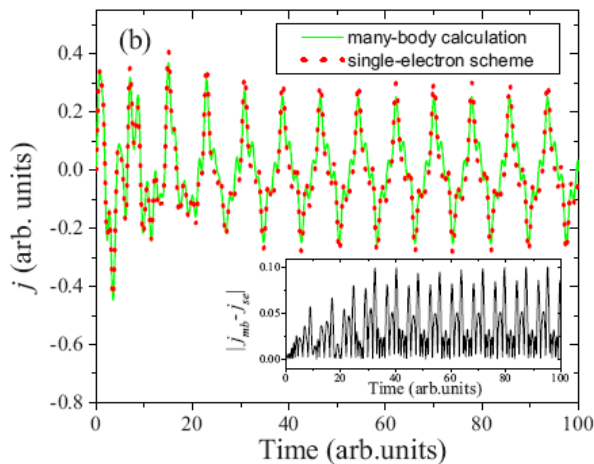
[Pershin, Dubi & Di Ventra, PRB **78**, 054302 (2008)]

An open Quantum System Approach

Comparison between full Many-Body and Single-Particle equations:

<u>Example 2</u> – Linear chain with two temperatures

$$\dot{\hat{\rho}} = -i[\mathcal{H}, \hat{\rho}] + \mathcal{L}_L \hat{\rho} + \mathcal{L}_R \hat{\rho}$$

$$\mathcal{H} = -\sum_{i,j} t_{i,j} |i\rangle\langle j|$$

$$V_{kk'}^{(L,R)} = \sqrt{\gamma_{kk'}^{(L,R)} \ f_D^{(L,R)}(\varepsilon_k)} |k\rangle\langle k'|$$

$$\gamma_{kk'}^{(L,R)} = \gamma_0 \int_{S_{L,R}} \mathrm{d}r \, |\psi_k(r)\|\psi_{k'}(r)|$$

$$f_D^{(L,R)}(\varepsilon_k) = \cfrac{1}{\exp\left(\cfrac{\varepsilon_k - \mu_{L,R}}{T_{L,R}}\right) + 1}$$

Thermo-electric effects in a Nano Junction

$$\dot{\hat{\rho}} = -i[\mathcal{H}, \hat{\rho}] + \mathcal{L}_L \hat{\rho} + \mathcal{L}_R \hat{\rho}$$

| Geometry Interactions | Temperature From Left | Temperature From Right |
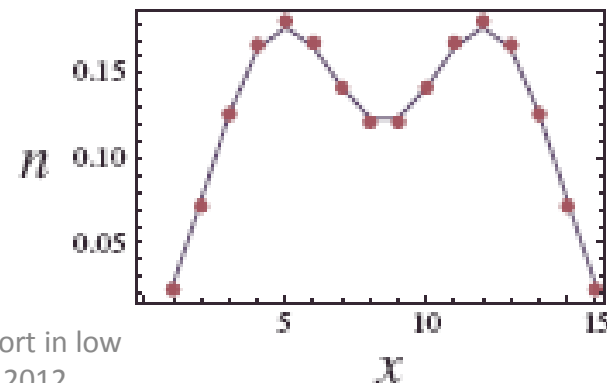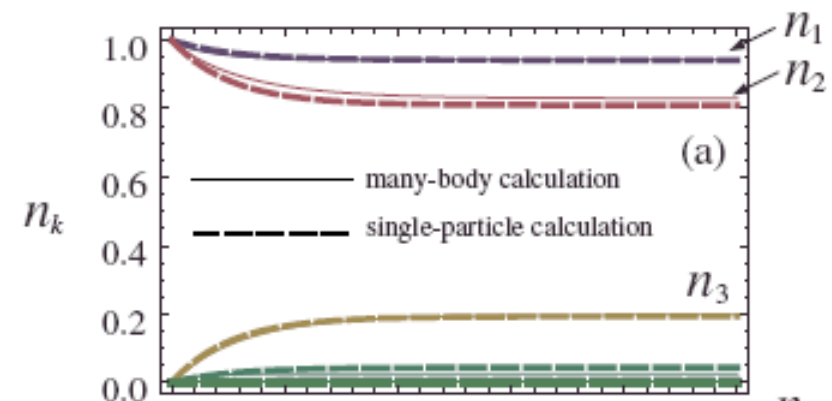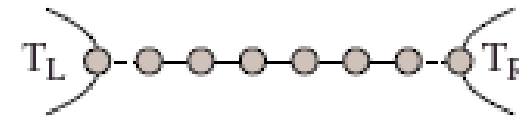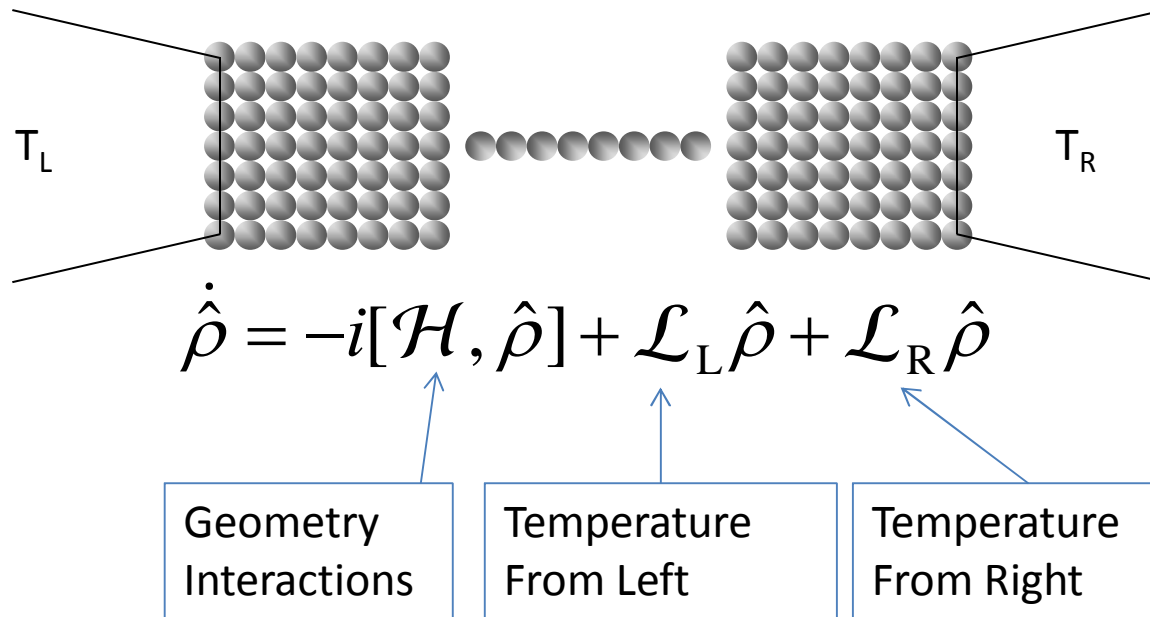
DFT	Open Quantum System (OQS)
ground state	finite T
equilibrium	non-equilibrium
extended by TD-DFT	extends TD-DFT
first Principles	phenomenological parameter
	additional computational cost

Thermo-electric effects in a Nano Junction

$L_x \times L_y = 28 \times 27$

$L_d = 4$

$n \sim 0.45$ (slightly below half-filling) T_L

$g_L = g_R = 0.1$

$T_L = RT$

ε_{gate}

T_R
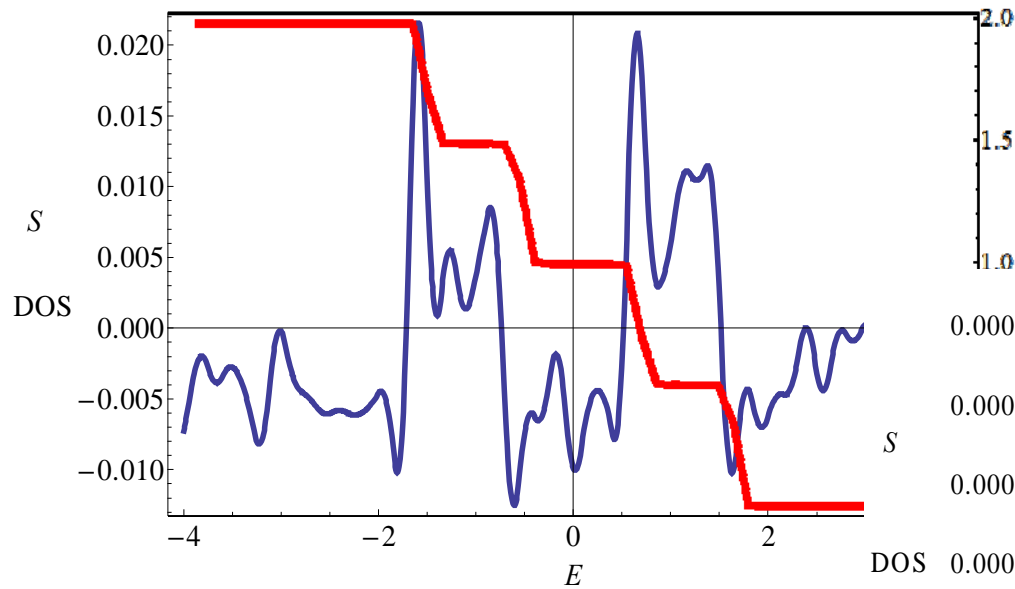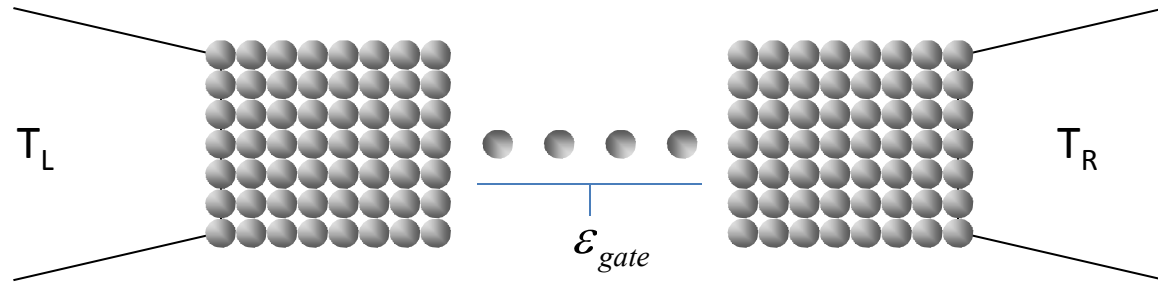
Landauer resonant level:
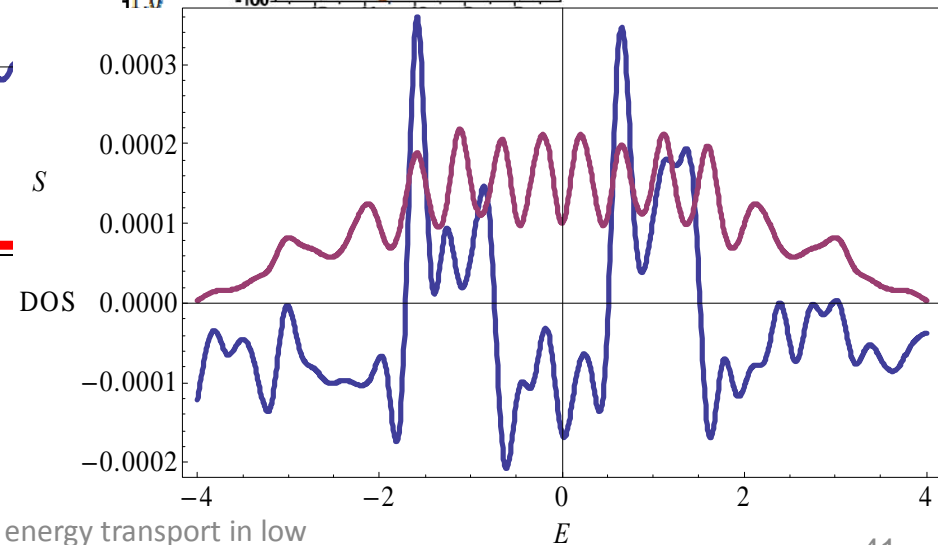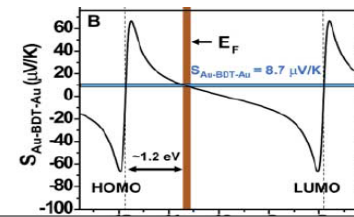
Thermo-electric effects in a Nano Junction

$L_x \times L_y = 20 \times 19$

$L_d = 2$

$n \sim 0.45$ (slightly below half - filling) T_L

$g_L = g_R = 0.1$

$T_L = RT$

ε_{gate}

T_R
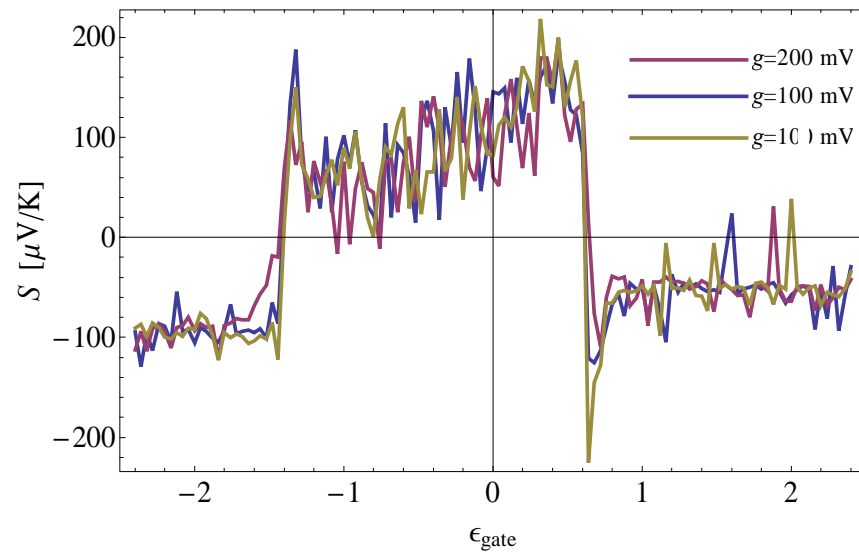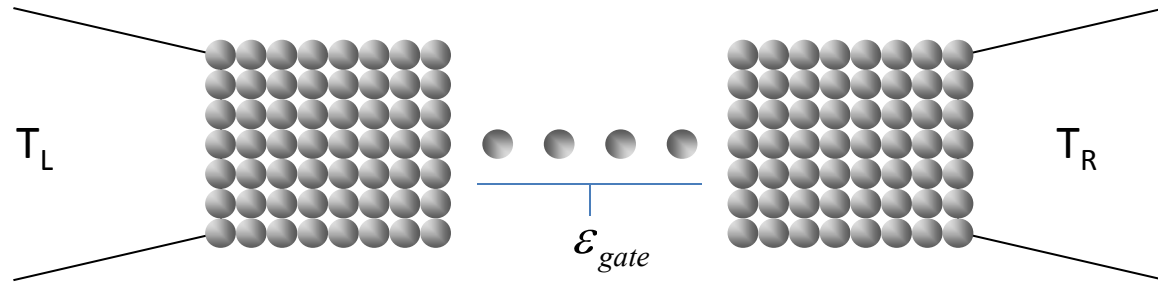
of the HOMO to the chemical potential. We also show that when the coupling of the molecule with one of the electrodes is reduced, the electrical conductance of junctions decreases dramatically, whereas the thermopower remains relatively invariant. Further, we show that

Tan, Dunitz, Reddy *et al.*,
JACS **133,** 8838 (2011)

Thermo-electric effects in a Nano Junction

Non-homogeneous *T*-dependence
(coherent tunneling Vs. thermal activation)
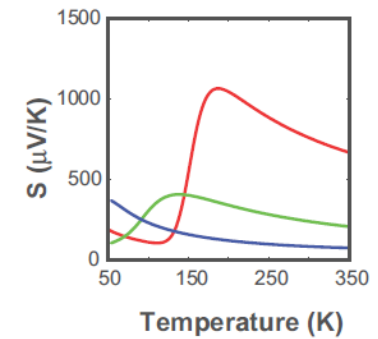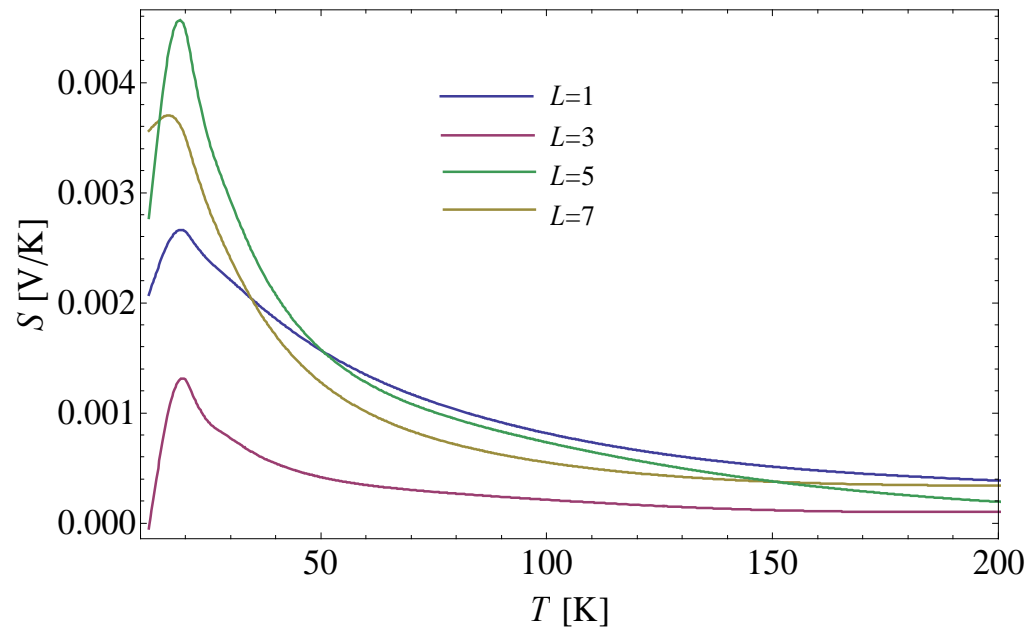
D. Nozaki *et al.*, PRB **81**, 235406 (2010)
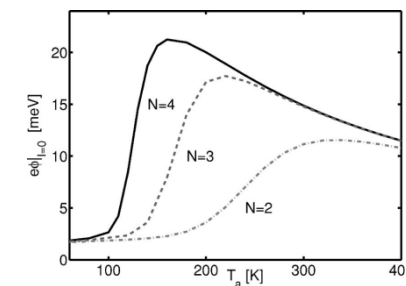
D. Segal, PRB **72**, 165426 (2005)

Thermo-electric effects in a Nano Junction

Fluctuations in an atomic wire:

Increasing piezovoltage
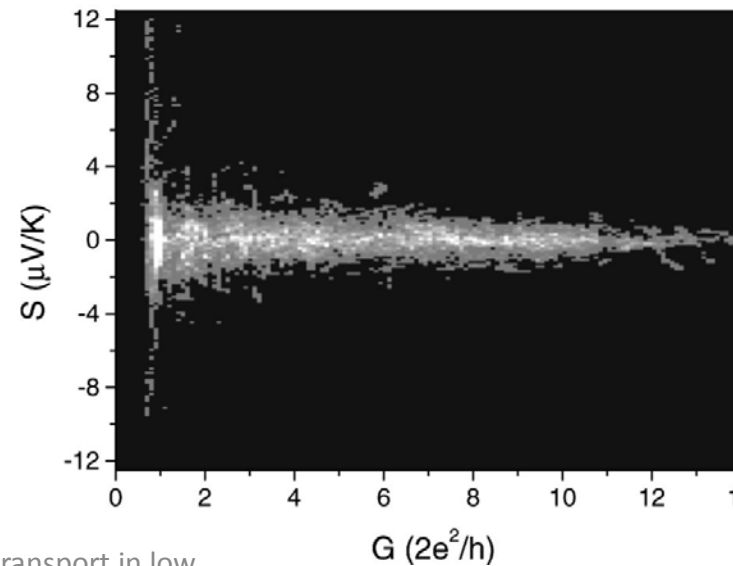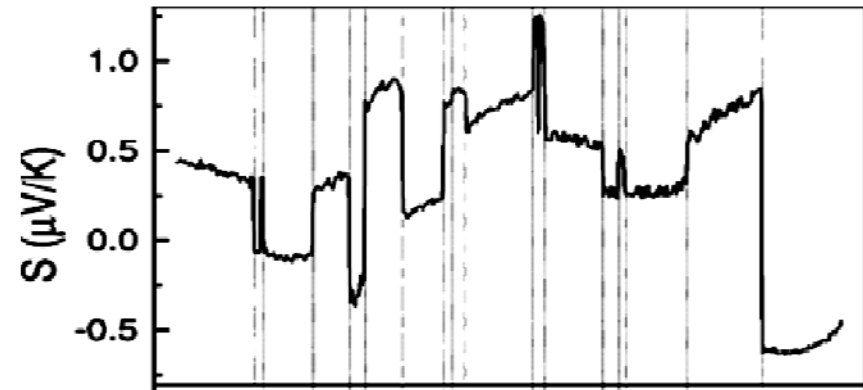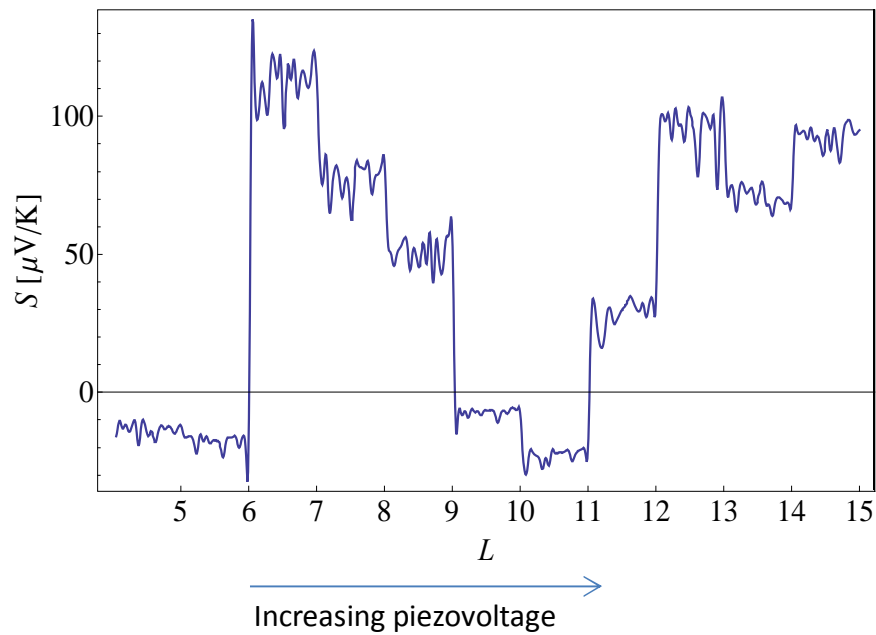
Thermo-electric effects in a Nano Junction

$L_x \times L_y = 20 \times 19$

$n \sim 0.45$ (slightly below half - filling)

$g_L = g_R = 0.1$

$T_L = RT$

$\delta T = 2K, \ \sigma_{gate} = 0.2 eV$
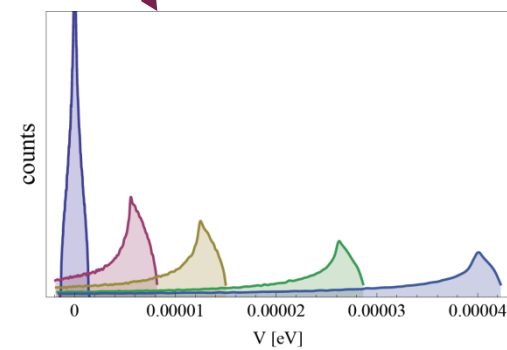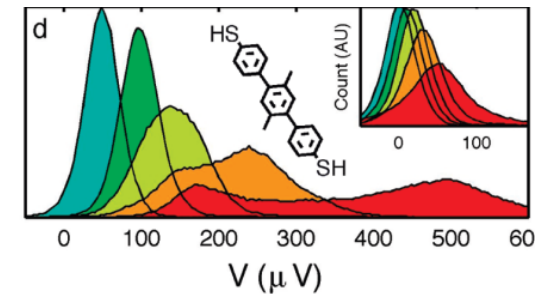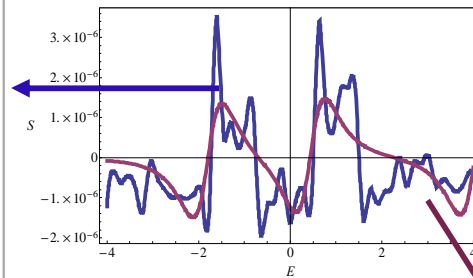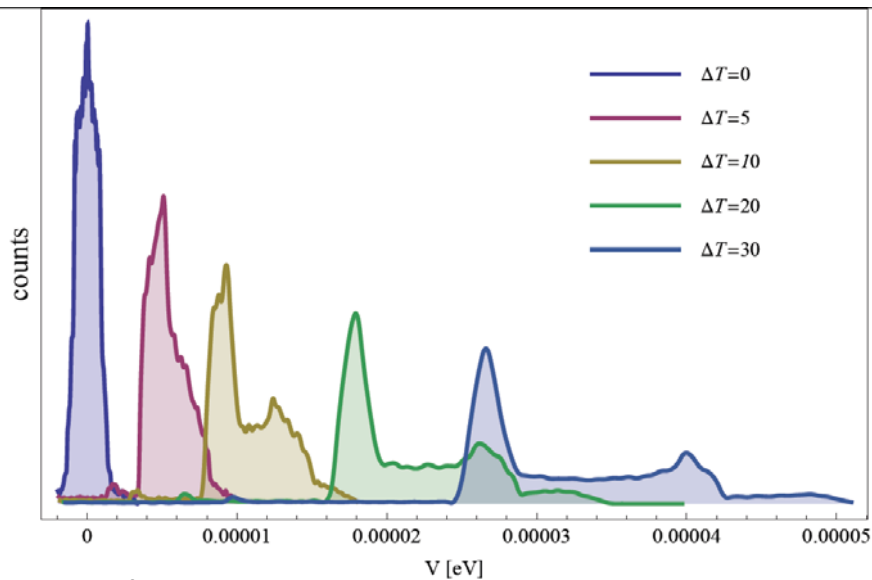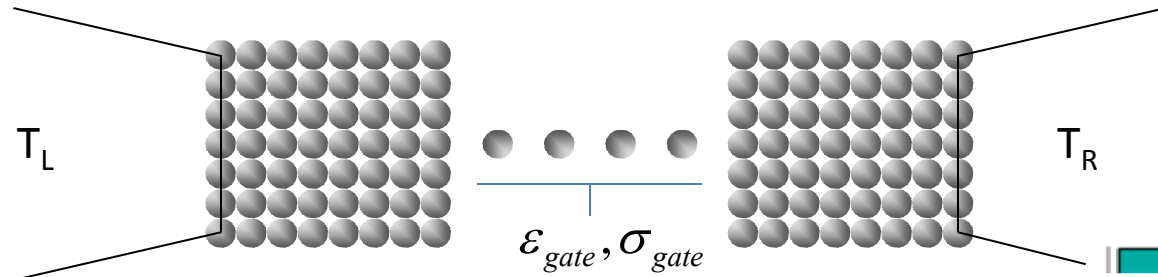
Conclusion:

LDOS fluctuations at molecule-electrode interface are essential

Thermo-electric effects in a Nano Junction

Effect of disorder - an open question

Effect of interaction?
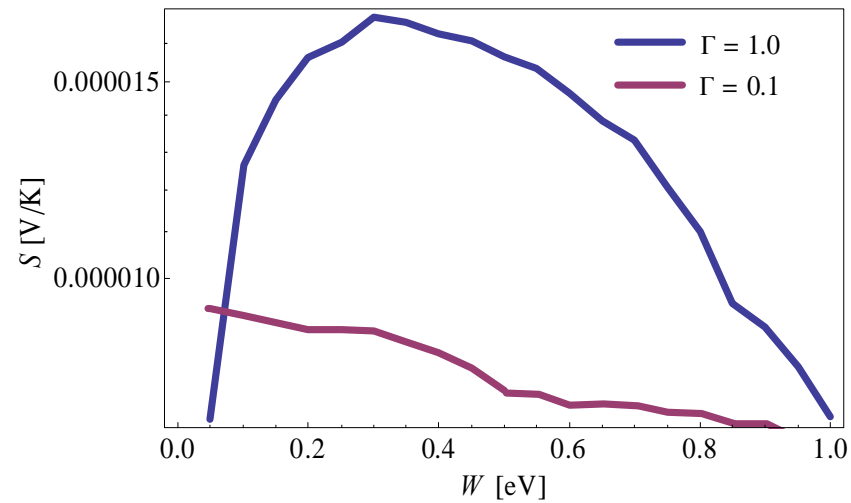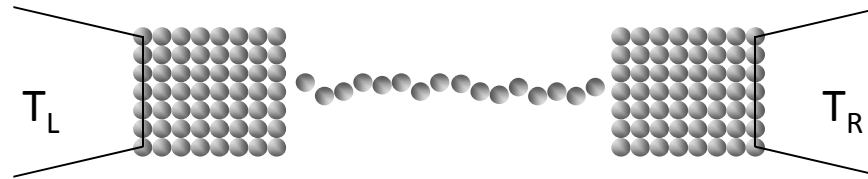
Landauer's formula:
Opposite prediction
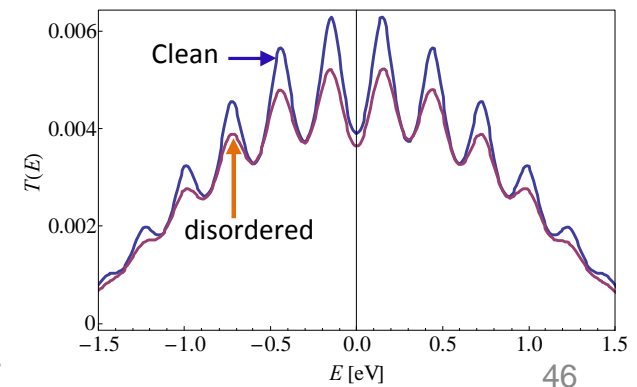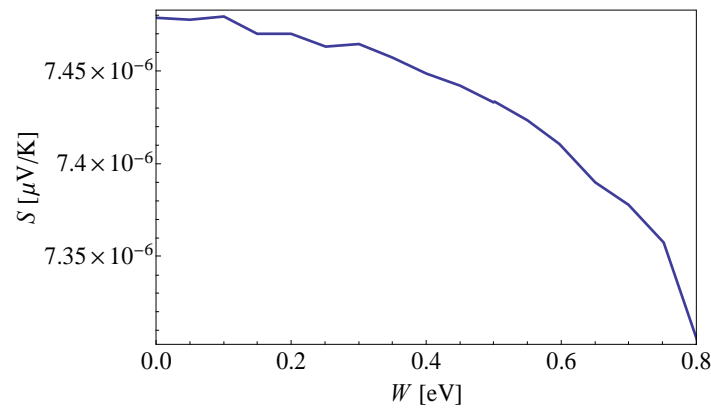
Energy transport in **electronic** nano- and molecular junctions

Yonatan Dubi

Ben-Gurion University of the Negev

ISRAEL

$$\partial_t \Psi(\mathbf{r},t) = -i\hat{H}(t)\Psi(\mathbf{r},t) - \tfrac{1}{2}\hat{V}^+\hat{V}\Psi(\mathbf{r},t) + \hat{V}\, l(t)\Psi(\mathbf{r},t)$$

Wave-
function

System
(geometry,
interactions)

Environment (temperature(s))

Equivalent to:

$$\dot{\hat{\rho}}_{MB} = -i[\mathcal{H},\hat{\rho}_{MB}] + \mathcal{L}\hat{\rho}_{MB}$$

$$\mathcal{L}\hat{\rho}_{MB} = \sum_i \left(V_i \hat{\rho}_{MB} V_i^+ - \tfrac{1}{2}\{V_i^+ V_i, \hat{\rho}_{MB}\} \right)$$

If the bath is Ohmic and Markovian we have intuition into its operation:

$$V_{k,k\prime} = \gamma_{kk\prime}(r)|\Psi_k\rangle\langle\Psi_{k\prime}|, \qquad \frac{\gamma_{kk\prime}}{\gamma_{k\prime k}} \propto \exp\left(-\frac{\Delta E_{kk\prime}}{k_B T}\right)$$

In the non-interacting limit: a mapping to single-particle

$$\dot{\hat{\rho}} = -i[\mathcal{H},\hat{\rho}] + \mathcal{L}\rho$$

$$\hat{\rho}_{kk'} = \mathrm{Tr}(c_k^+ c_k \rho_M)$$

$$\mathcal{L}\hat{\rho} = -\tfrac{1}{2}\{V^+ V, \hat{\rho}\} + V\rho V^+$$

$$V_{kk'}^{(\mathrm{L,R})} = \sqrt{\gamma_{kk'}\, f_D(\varepsilon_k)}\,|k\rangle\langle k'|$$

$$\gamma_{kk'}^{(L,R)} = \gamma_0 \int_{S_{\mathrm{L,R}}} dr\, |\psi_k(r)\| \psi_{k'}(r)|, \qquad f_D^{(L,R)}(\varepsilon_k) = \dfrac{1}{\exp\left(\dfrac{\varepsilon_k - \mu_{L,R}}{T_{L,R}}\right)+1}$$

$L_x \times L_y = 28 \times 27$

$L_d = 4$

$n \sim 0.45$ (slightly below half - filling) T_L

$g_L = g_R = 0.1$

$T_L = RT$
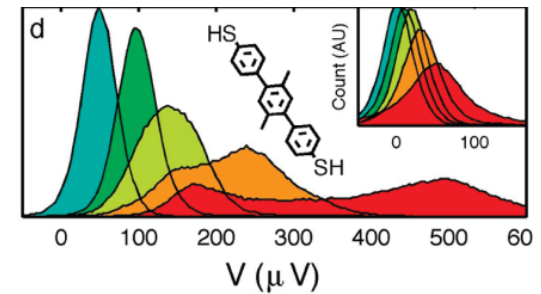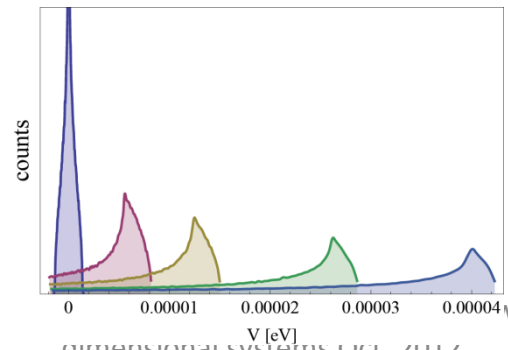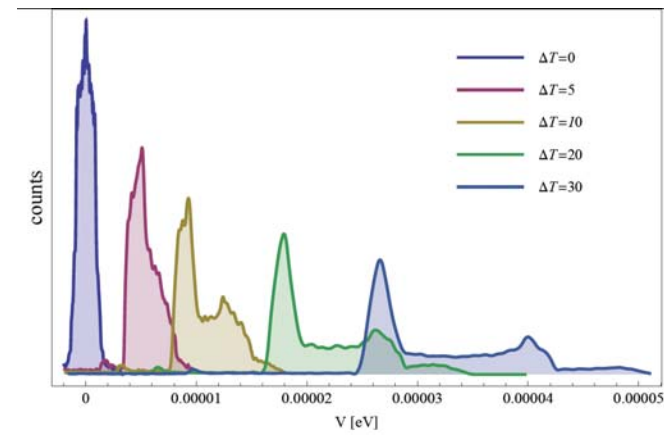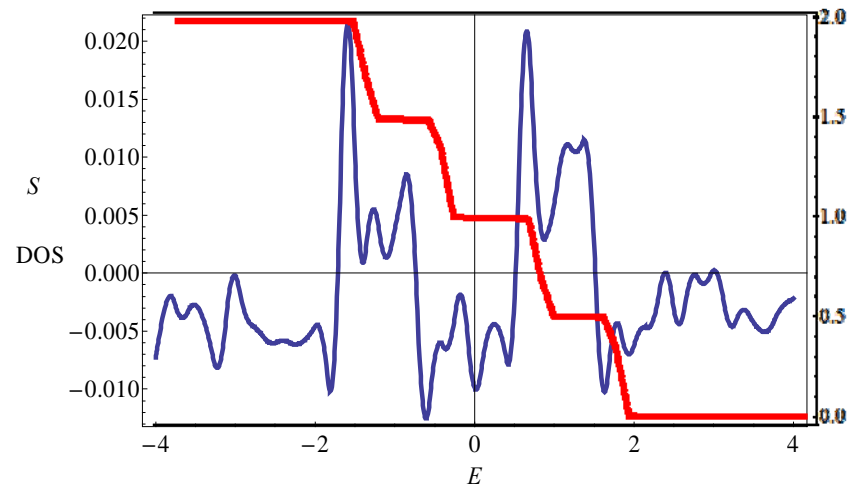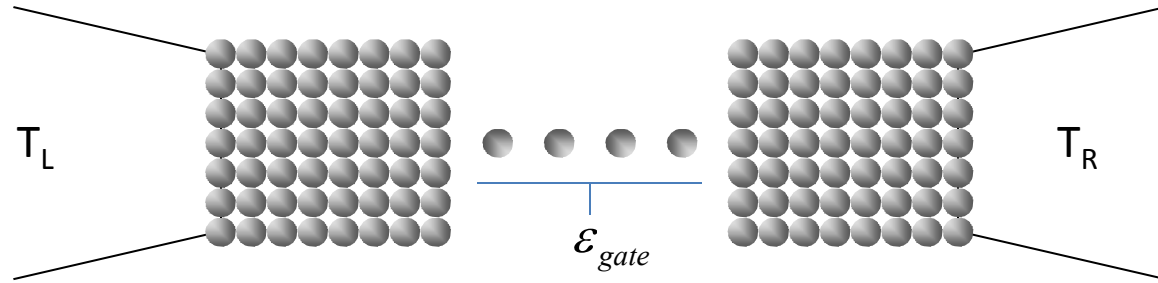
Local temperature in a Nano Junction

How to calculate temperature locally? Same way as it is measured!

$$\dot{\hat{\rho}} = -i[\mathcal{H}, \hat{\rho}] + \mathcal{L}_L \hat{\rho} + \mathcal{L}_R \hat{\rho} + \mathcal{L}_{tip} \hat{\rho}$$
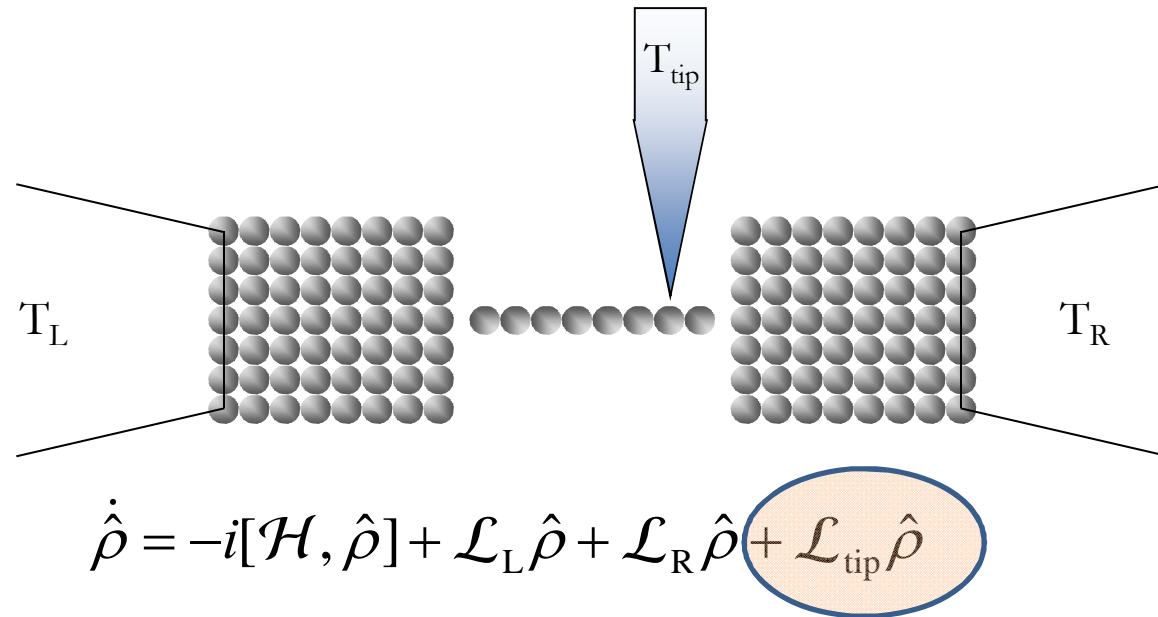
- Scan T_{tip}

- T(r) is T_{tip} for which local properties are the same in the absence of tip

- No heat flowing between the sample and the tip

Local temperature in a Nano Junction

Is this method any good?
Test : a two level quantum dot

- calculate occupation via rate equations
- Sequential tunneling approx.
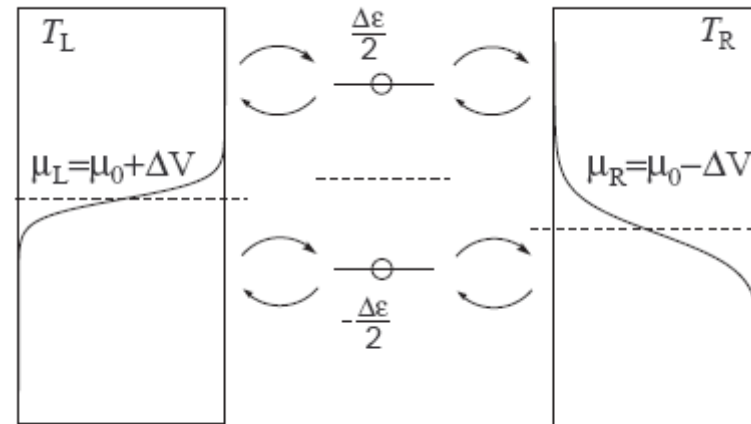
$$\begin{pmatrix} \dot{p}_0(t) \\ \dot{p}_1(t) \\ \dot{p}_2(t) \end{pmatrix} = \begin{pmatrix} -W_{10} - W_{20} & W_{01} & W_{02} \\ W_{10} & -W_{01} & 0 \\ W_{20} & 0 & -W_{02} \end{pmatrix} \begin{pmatrix} p_0(t) \\ p_1(t) \\ p_2(t) \end{pmatrix}$$

$$W_{n0} = \sum_{\nu=L,R} W_{n0}^{\nu} = \sum_{\nu=L,R} a_{\nu}(1 - f_{\nu}(\epsilon_n)),$$

$$W_{0n} = \sum_{\nu=L,R} W_{0n}^{\nu} = \sum_{\nu=L,R} a_{\nu} f_{\nu}(\epsilon_n), \quad n = 1, 2$$

1st way to define T_{eff} :

$$\frac{p_2}{p_1} = \exp\left(-\frac{\Delta\epsilon}{T_{\text{eff}}}\right)$$

Local temperature in a Nano Junction

2nd way to define T_{eff} :

1. Include an additional tip with temperature T_{tip}

$$\left(\frac{p_2}{p_1}\right)_{\text{tip}} - \frac{f_L(\epsilon_1) + f_R(\epsilon_1) + f_{\text{tip}}(\epsilon_1)}{3 - f_L(\epsilon_1) - f_R(\epsilon_1) - f_{\text{tip}}(\epsilon_1)} \frac{3 - f_L(\epsilon_2) - f_R(\epsilon_2) - f_{\text{tip}}(\epsilon_2)}{f_L(\epsilon_2) + f_R(\epsilon_2) + f_{\text{tip}}(\epsilon_2)}$$

2. Make sure the tip doesn't change anything

$$\left(\frac{p_2}{p_1}\right)_{\text{tip}} - \frac{p_2}{p_1} = 0$$

Local temperature in a Nano Junction

g

T_L

T_R

T_{tip}
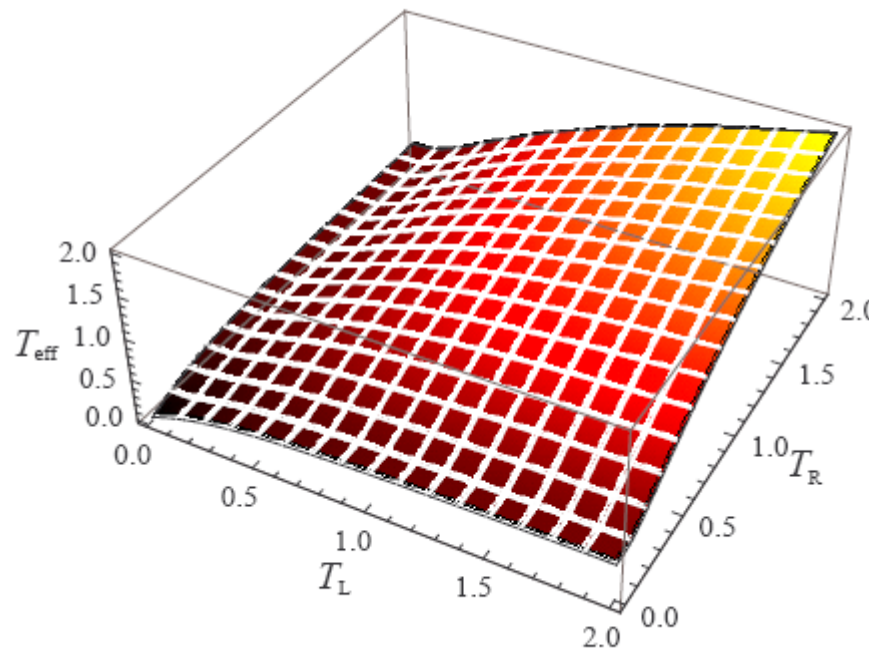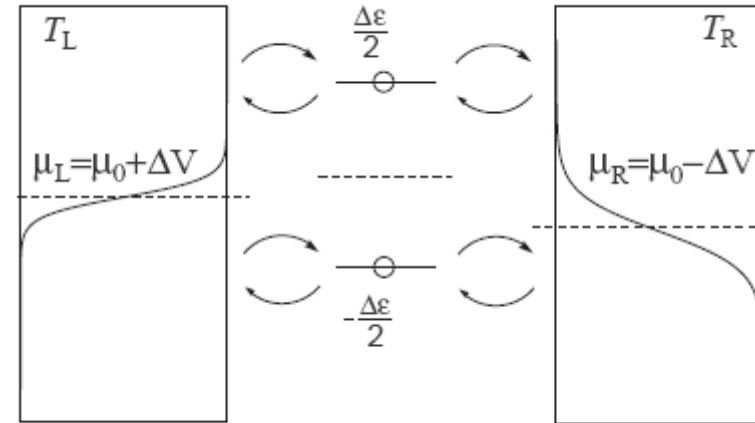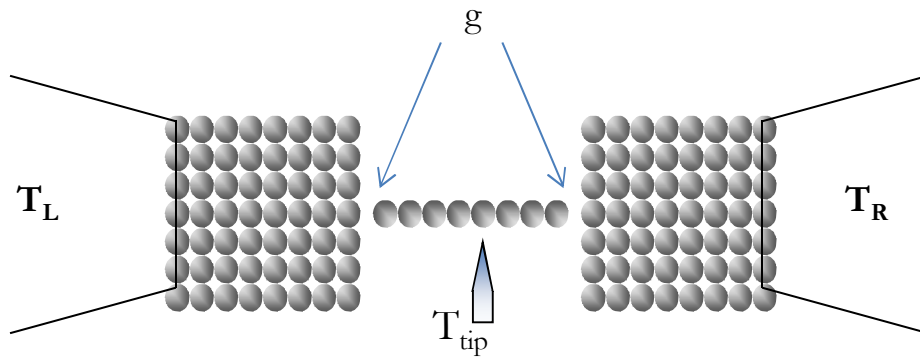
- Small g – lower temperature better coupled to wire

- Intermediate g – Temperature oscillations

- Large g – Uniform Temperature

g

g

$g=1$

$g=0.1$

$g=0.01$

$T_L=0.1$

$L_d=50$

$T_R=1$

$L_x=L_y=5$
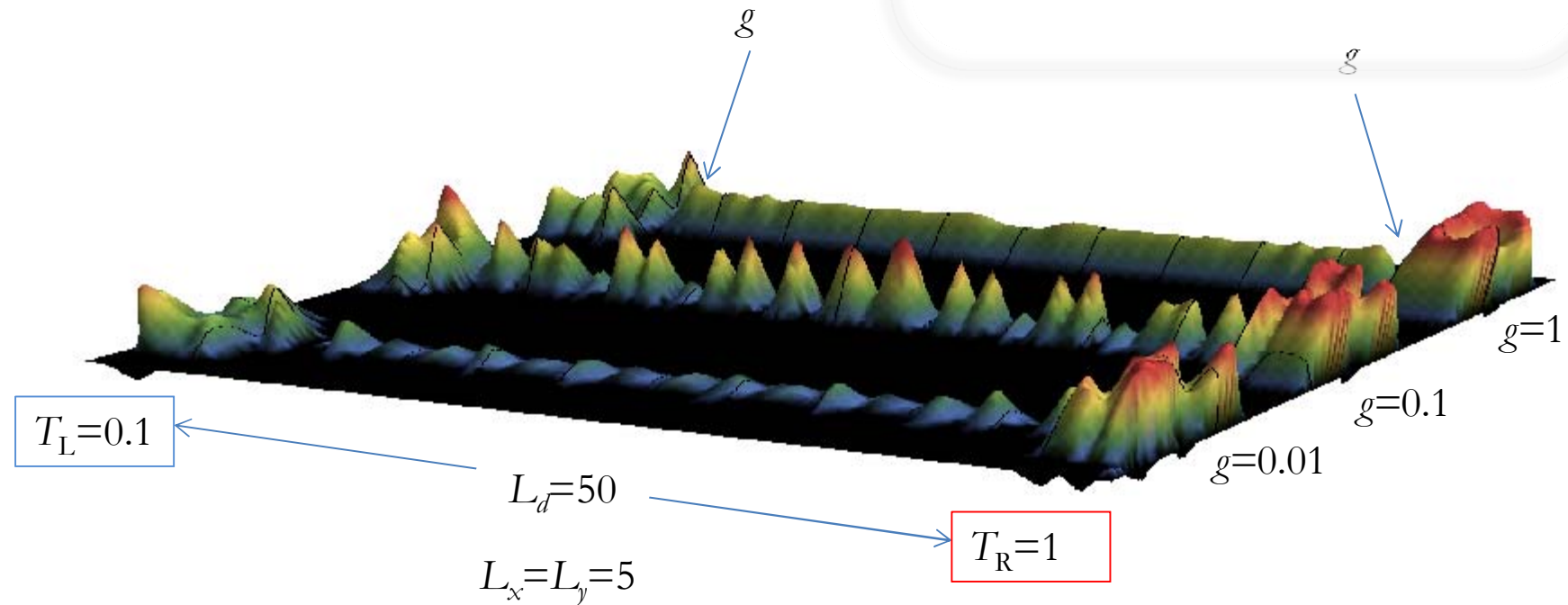
J. B. J. Fourier
(1768 – 1830)

$$j = -k\nabla T$$

Energy current

Thermal conductivity

Temp. gradient

~200 years later…

FOURIER LAW: A CHALLENGE TO THEORISTS

F. BONETTO   J. L. LEBOWITZ   L. REY-BELLET

We present a selective overview of the current state of our knowledge (more precisely of our ignorance) regarding the derivation of Fourier's Law, $\mathbf{J}(\mathbf{r}) = -\kappa\nabla T(\mathbf{r})$: $\mathbf{J}$ the heat flux, T the temperature and κ, the heat conductivity. This law is empirically well tested for both fluids and crystals, when the temperature varies slowly on the microscopic scale, with κ an intrinsic property which depends only on the system's equilibrium parameters, such as the local temperature and density. There is however at present no rigorous mathematical derivation of Fourier's law and ipso facto of Kubo's formula for κ, involving integrals over equilibrium time correlations, for any system (or model) with a deterministic, *e.g.* Hamiltonian, microscopic evolution.

[Bonetto, Lebowitz & Rey-Bellet,
Mathematical Physics 2000
(Imperial College, London, 2000)]
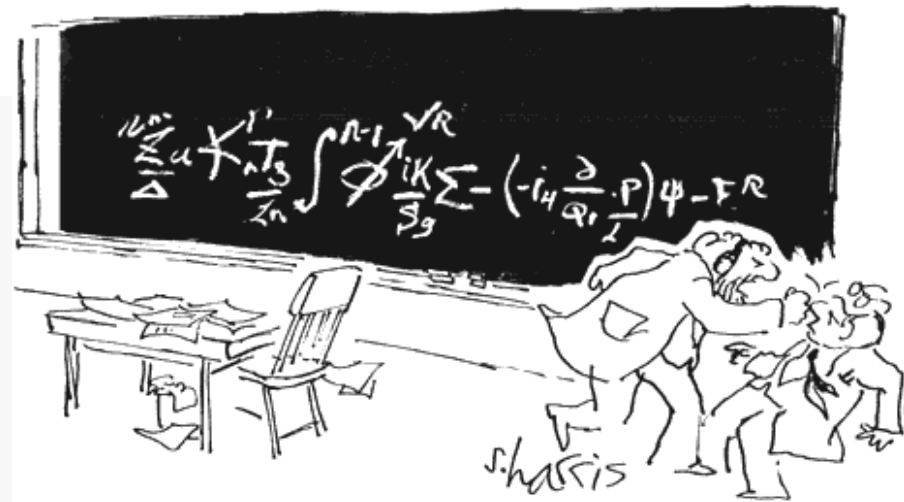
"You want proof? I'll give you proof!"

Reconstructing Fourier's law from disorder
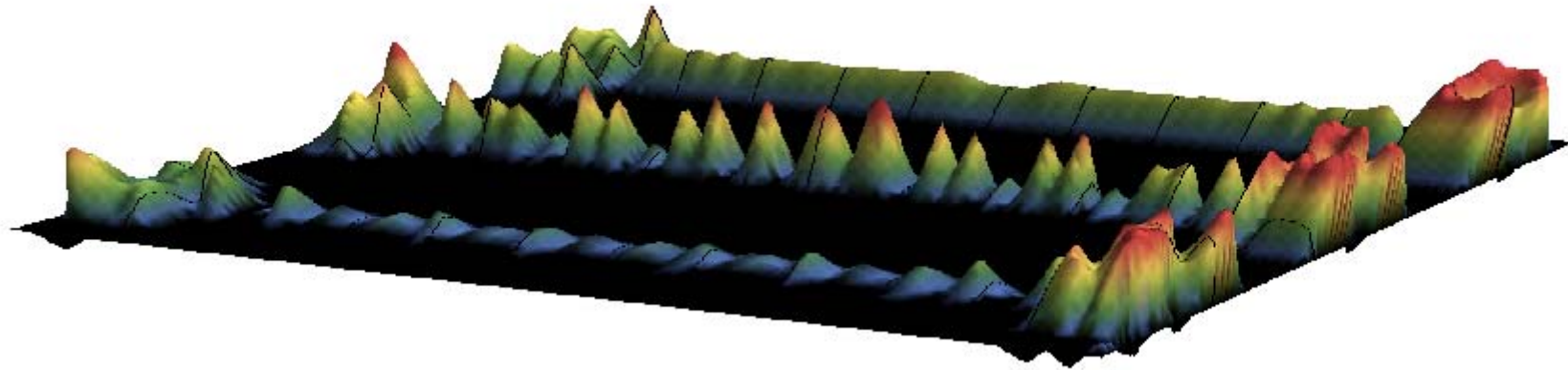
Breakdown of Fourier's law in

ballistic quantum wires

[Dubi & Di Ventra,
Nano letters **9,** 97 (2009)]

Reconstructing Fourier's law from disorder

$$\mathcal{H} = -\sum_{i,j} t_{i,j} |i\rangle\langle j| + \sum_{i} \epsilon_i |i\rangle\langle i|, \qquad \epsilon_i \in N[0, W]$$
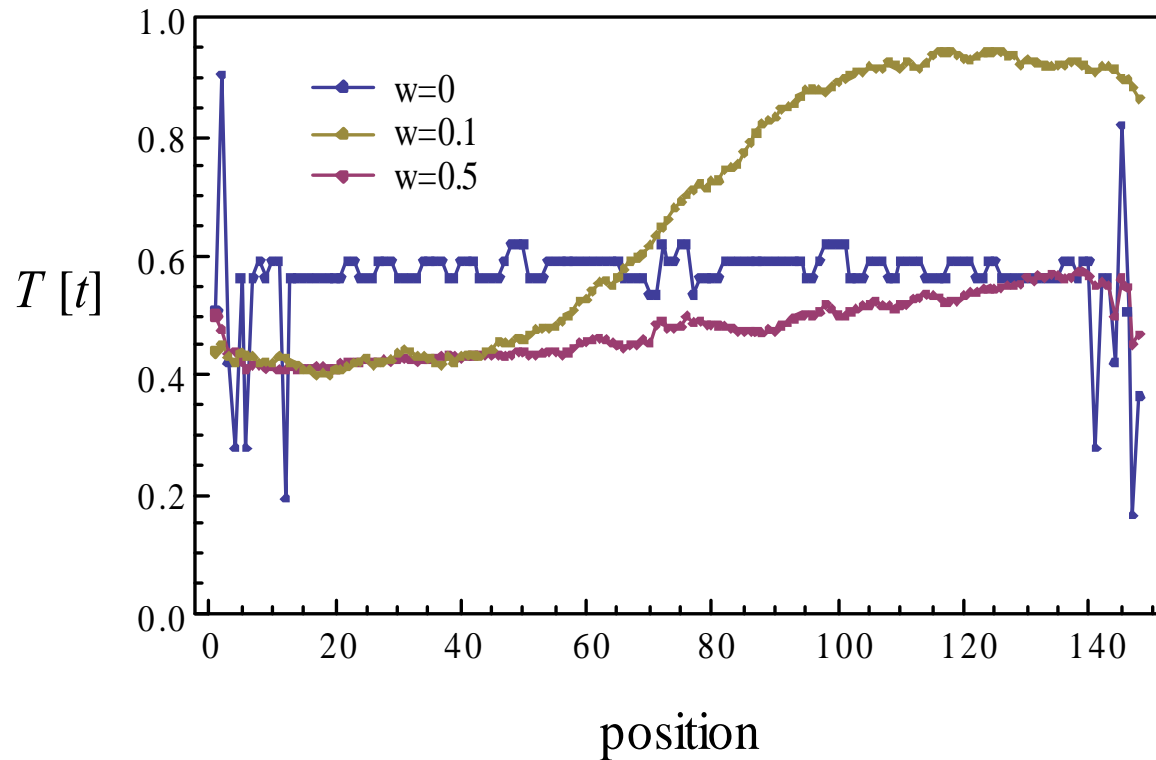
Fourier's law is reconstructed by disorder

(it seems to fit the onset of "Quantum Chaos")
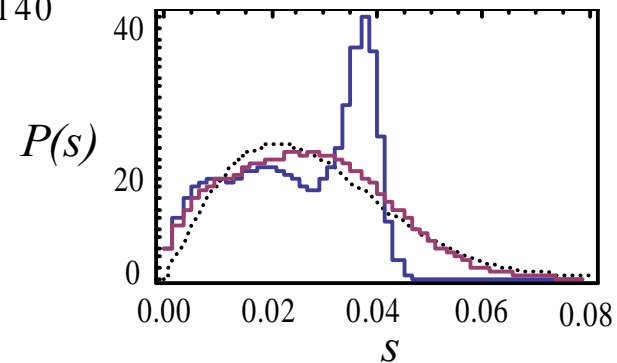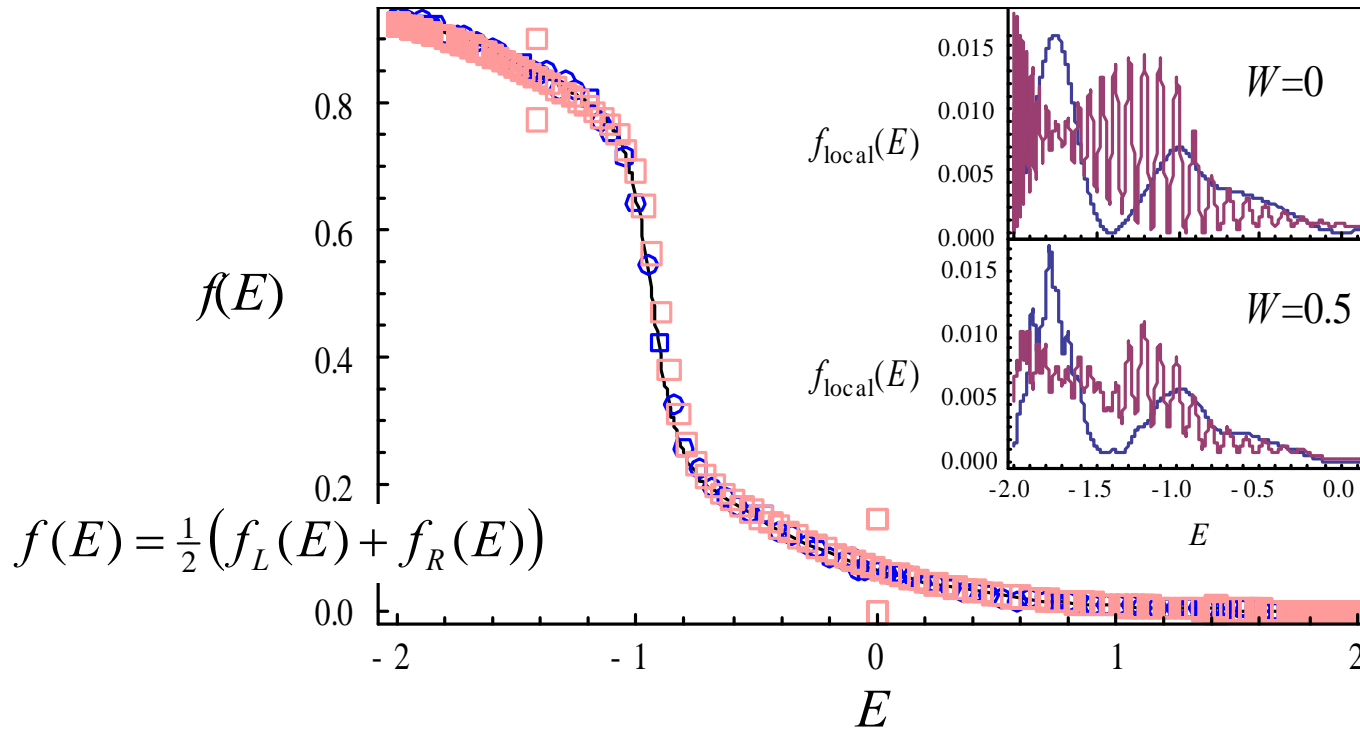
Reconstructing Fourier's law from disorder

Local heat current and thermal conductivity
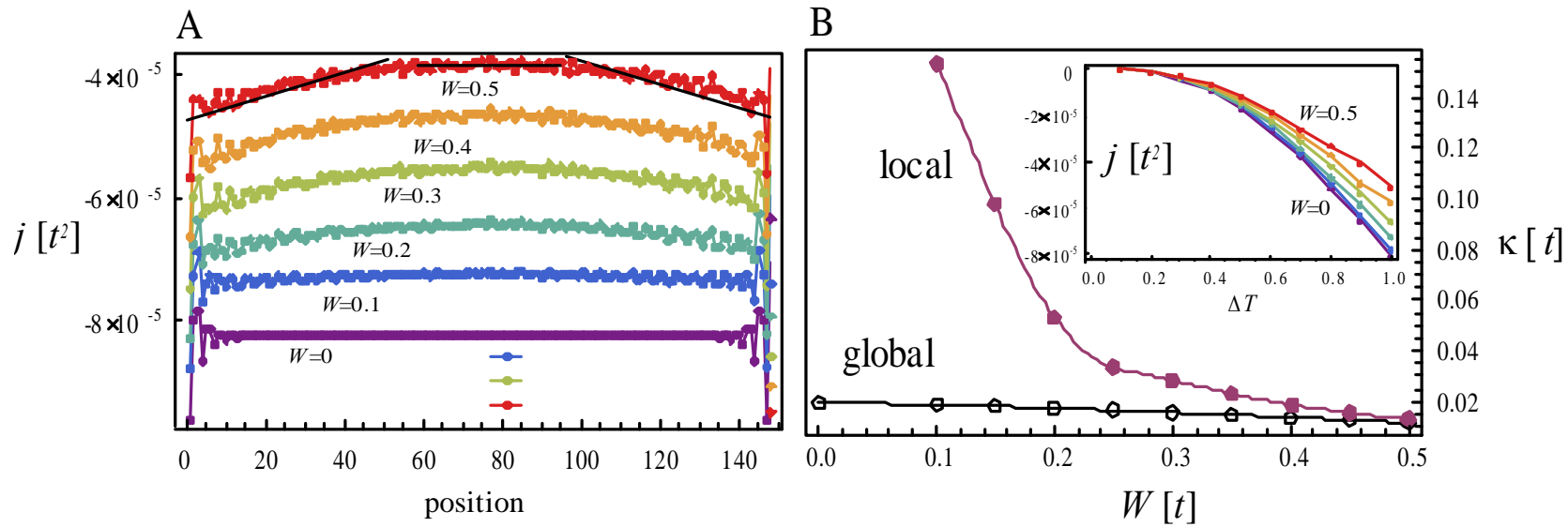
$$\kappa_{local} = \frac{j_{local}}{\nabla T_{local}}$$

$$\kappa_{global} = \frac{\bar{j}}{(T_L - T_R)/L}$$

Role of disorder

Energy distribution function :

$$f(E) = \tfrac{1}{2}\left(f_L(E) + f_R(E)\right)$$

(Master equation
+diagonal disorder)

Insight from a simple model

Assumptions :

1. T_L and T_R fixed

2. Local equilibrium

3. Weak coupling

"definition" of T: $\quad \dfrac{W_{k \to k'}}{W_{k' \to k}} = \exp\left(\dfrac{\Delta E_{kk'}}{k_B T} \right), \quad \forall k, k'$

Step 1: only S_L and S_1

$$W^{(1)}_{k \to k'} = \sum_{k_1, k_2} \Gamma^{1 \to L}_{k \to k_1} W^{(L)}_{k_1 \to k_2} \Gamma^{L \to 1}_{k_2 \to k'}$$

$$W^{(1)}_{k \to k'} = \gamma W^{(L)}_{k \to k'}$$
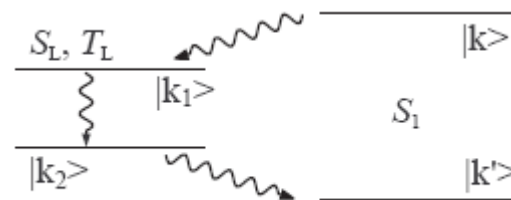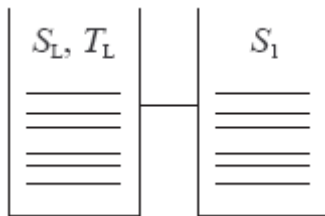
Insight from a simple model

Step 2: considering S_L and S_1, $S_2 \ldots S_n$ $\longrightarrow$ $W_{k \to k'}^{(n)} = \gamma^n W_{k \to k'}^{(L)}$

Step 3: considering full system with S_L and S_R $\longrightarrow$ $W_{k \to k'}^{(n)} = \gamma^n W_{k \to k'}^{(L)} + \gamma^{N-n} W_{k \to k'}^{(R)}$

Definition of T_n : $\dfrac{W_{k \to k'}^{(n)}}{W_{k' \to k}^{(n)}} \exp\left(\dfrac{\varDelta E_{kk'}}{k_B T_n} \right), \quad \forall k, k'$

$$T_n = T_L + \frac{1}{1 + \gamma^{2n-N}} \delta T$$

$$= T_L + \frac{1}{1 + \exp(x/\xi)} \delta T \quad , \xi = (N \log \gamma)^{-1}$$

$\left(x = \dfrac{2n}{N} - 1 \right)$
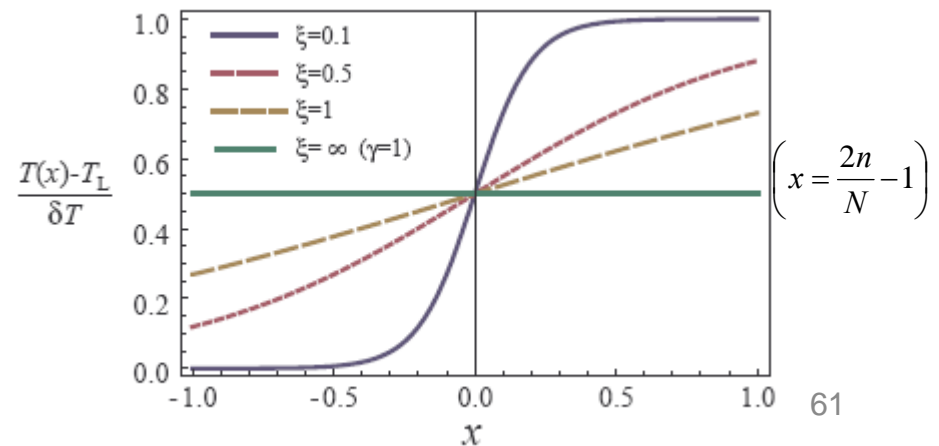
Insight from a simple model

$$T_n = T_L + \frac{1}{1+\exp(x/\xi)}\,\delta T$$
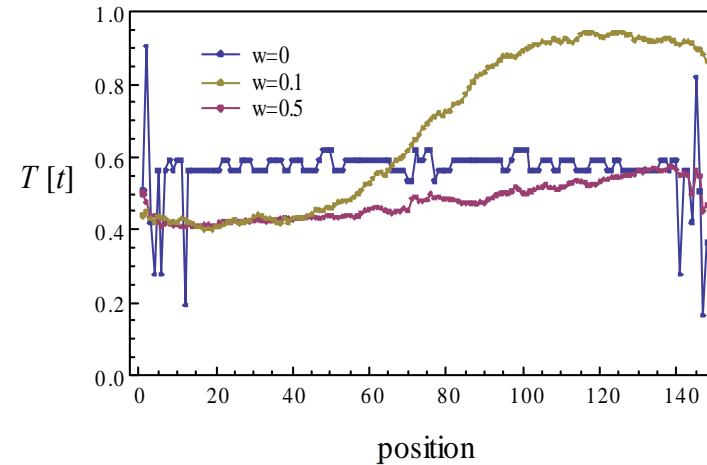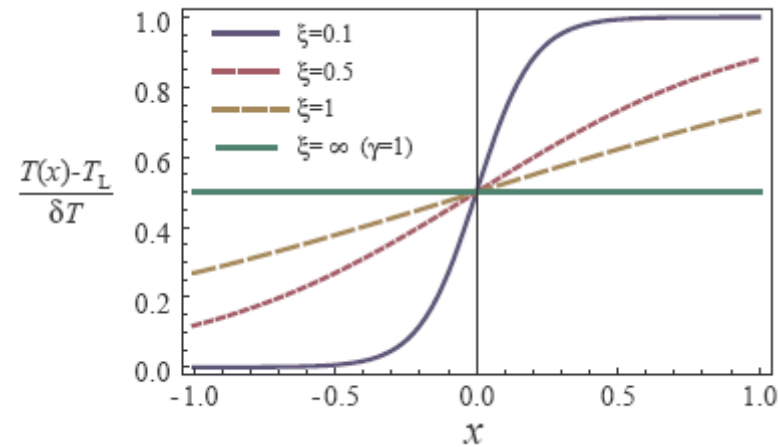
Interpretation :
 emergence of the length-scale ξ on which a local temperature exists

(if dephasing is included, L_φ replaces ξ and we get the classical Fourier's law :

$$T_n = T_L + \frac{n}{N_{eff}}\,\delta T, \quad N_{eff} = \frac{N}{L_\varphi} \,)$$

SUMMARY:

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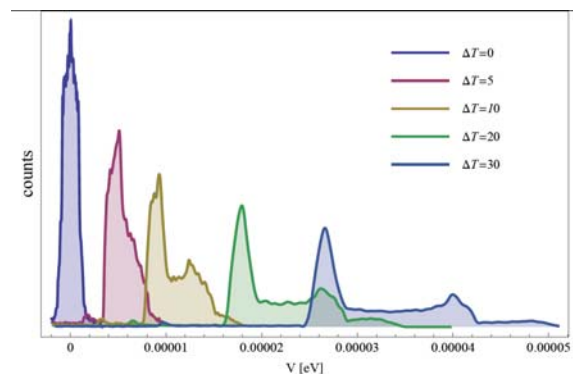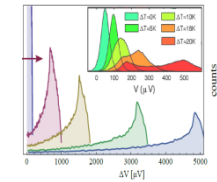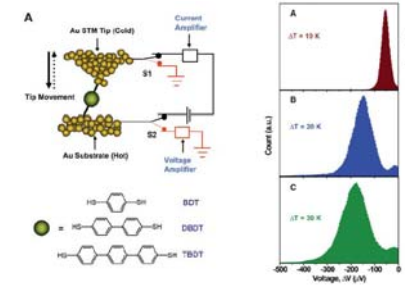- Conventional methods (rate equations, NEGF) seem to miss something…

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- 'Open Quantum systems' is a good approach to study TE in molecular junctions

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- Experiments of thermo-electricity in molecular junctions are certainly *achievements* and contain several *mysteries*

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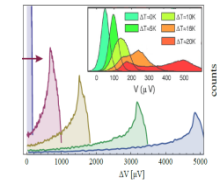- 'Open Quantum systems' is a good approach to study TE in molecular junctions

- And it can be used for other things too (e.g. local T)
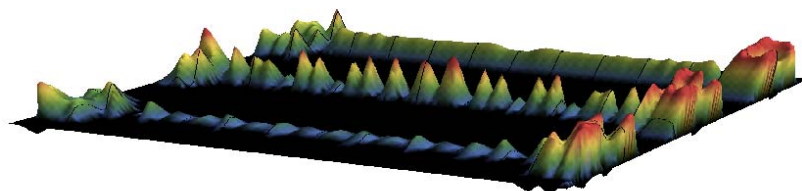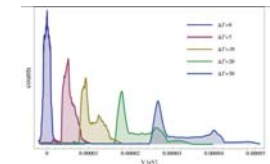
ADVANCED WORKSHOP ON ENERGY TRANSPORT IN LOW-DIMENSIONAL SYSTEMS: Achievements and Mysteries

15 - 24 October 2012
(ICTP, Miramare, Trieste, Italy)

Open questions:

- Origin of fluctuations in molecular junctions

- Phonon effects? Correlation effects?

- Combining DFT in a *good* way

- Is there a roadmap for increasing S ?