2371-17

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 I

Yonatan DUBI

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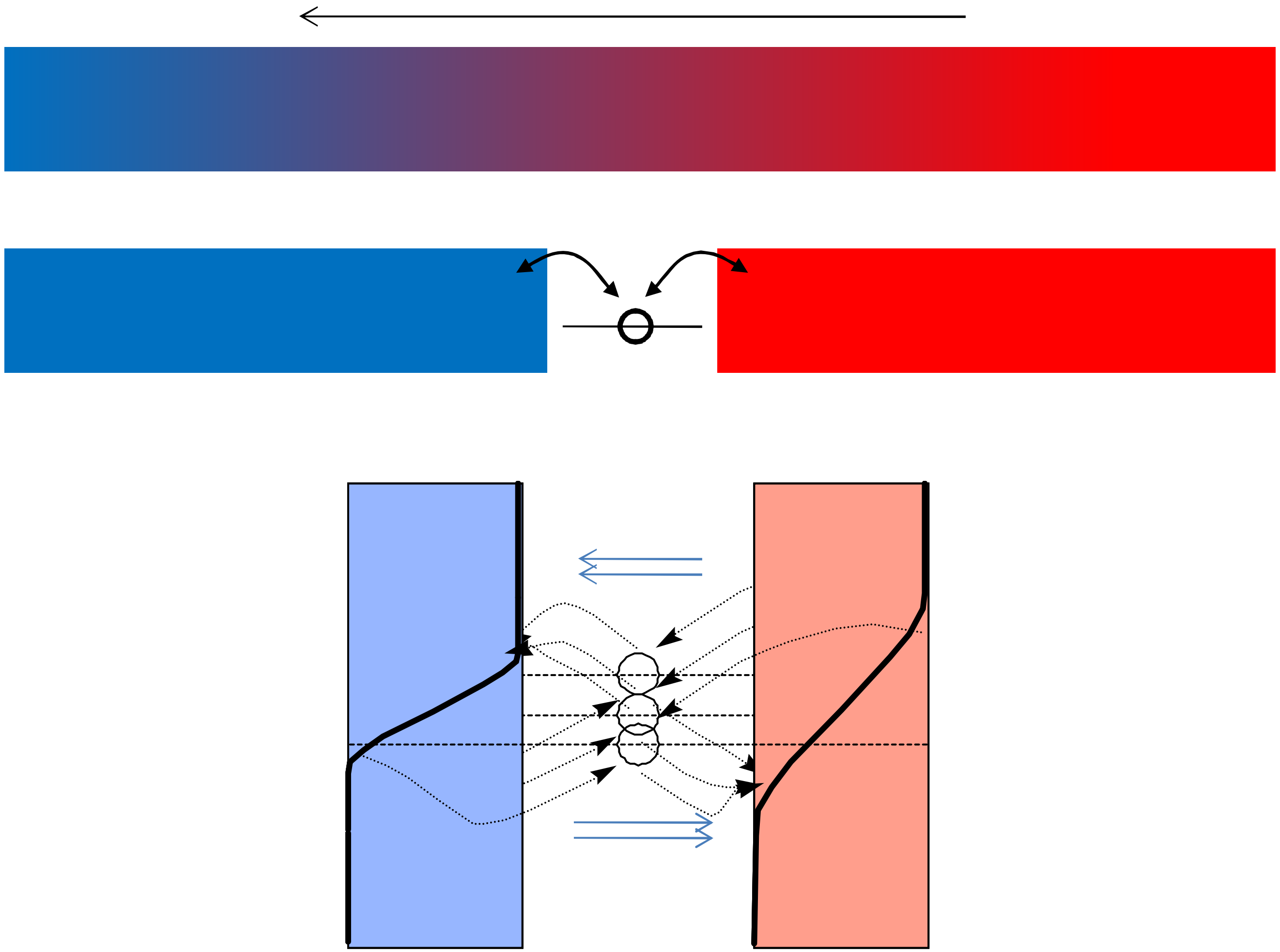
Energy transport in **electronic** nano- and molecular junctions

Yonatan Dubi
Ben-Gurion University of the Negev
ISRAEL

Teaser Trailer



Outline:

1. Introduction to energy transport in electronic nano- and molecular- junctions

   (mainly thermoelectricity!)

   i. State of the art experiments

   ii. What can we learn from them

2. Theoretical tools for studying thermo-power

   2.1 The rate equations method

   2.2 The Green's function method

   2.3 Open quantum systems approach

(3. Thermal transport through DNA nano-junctions)

A few remarks before we start:

1. Some of what I will say is not in text –books, but some is. Useful text-books are:

   M. Di-Ventra, *Nanoscale Quantum transport*.

   S. Datta, *Electronic transport in mesoscopic systems.*

   H. P. Breuer and F. Petrucionne, *The theory of open quantum systems.*

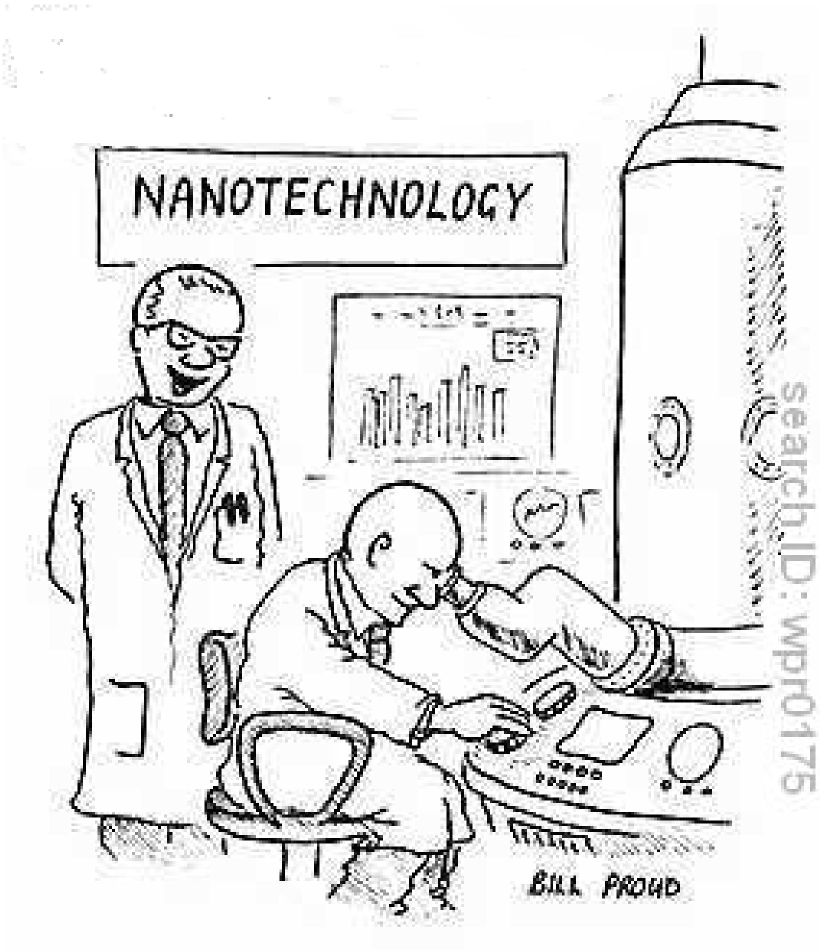
   Many review paper exist.

2. These are tutorial lectures. Please feel free to stop me and ask questions.

Part I

Introduction to energy transport in molecular- junctions

Motivation I: circuit miniaturization
(over-heating is devastating for molecular circuits)

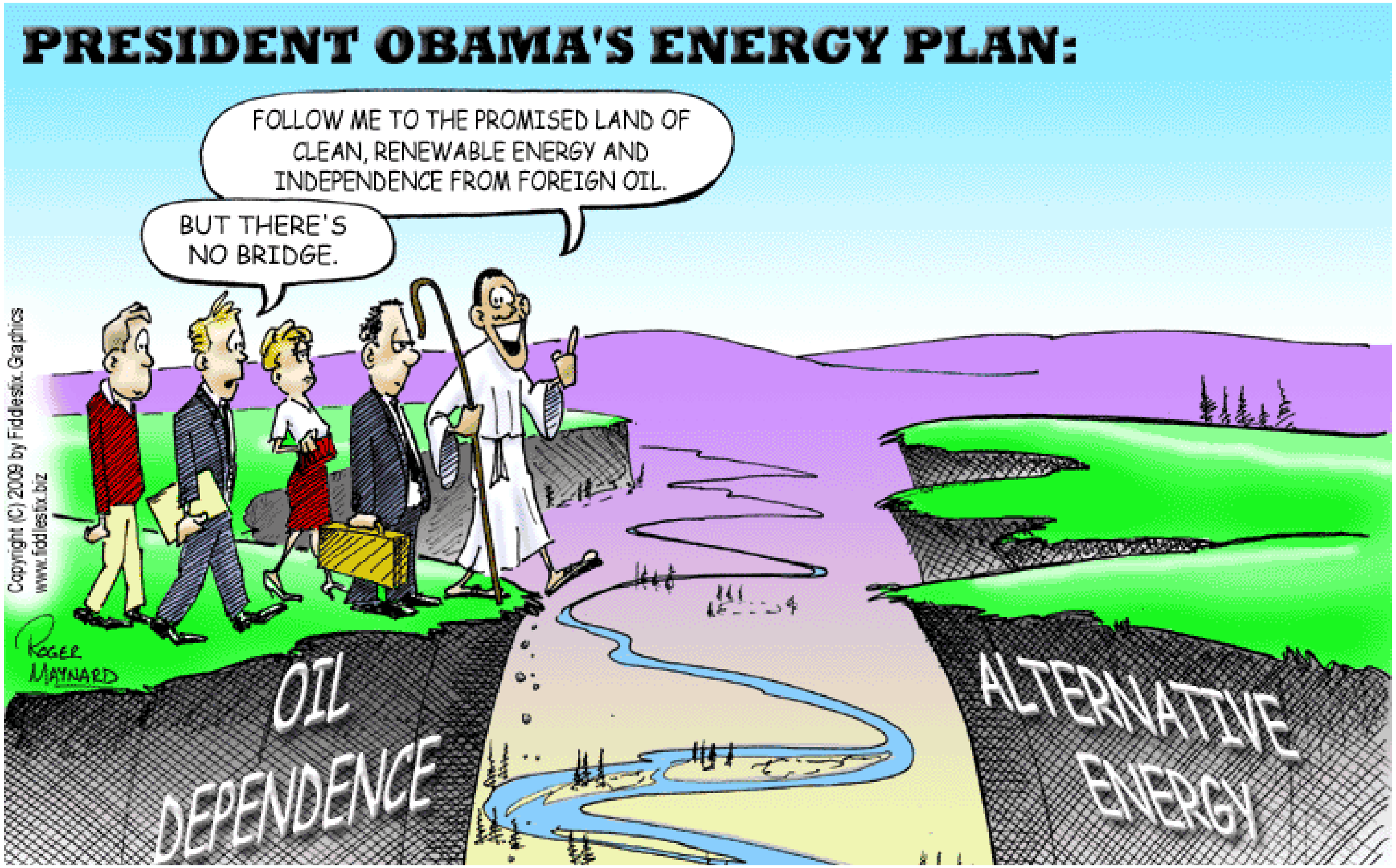


This is our new i-pod design...

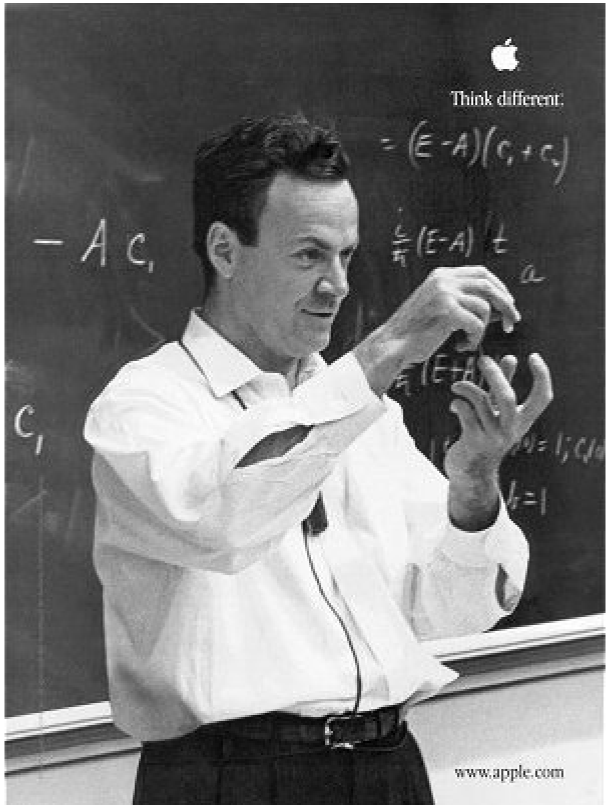
Motivation II: Energy

(Nano-elements may be used for Thermo-electric and other energy conversion)

Prof. Shakouri's tutorial!



Motivation III



"Physics is like sex: sure, it may give some practical results, but that's not why we do it."

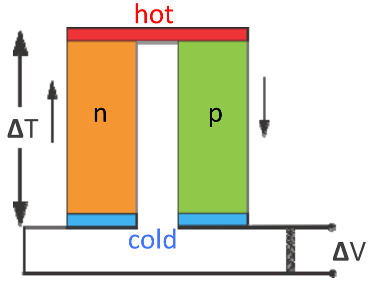
— Richard P. Feynman

Introduction: Thermo-electricity in molecular junction

T. J. Seebeck
1770-1831

Seebeck Effect :

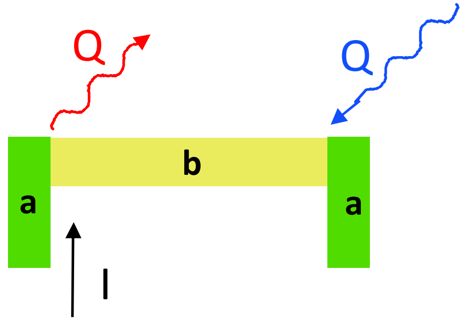
$$S = -\frac{\Delta V}{\Delta T}$$

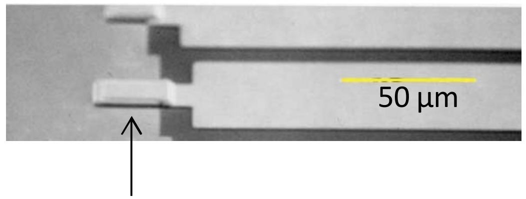


J. C. A.
Peltier
1785-1845

Peltier effect:

$$\pi_{ab} = \pi_a - \pi_b = \frac{Q}{I}$$

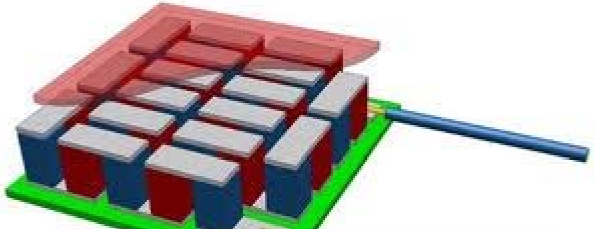


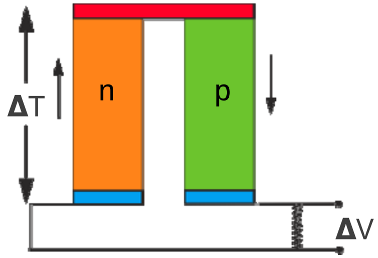


Can cool down by 40K (and more)

A. Shakouri, Proc. IEEE **94**, 1613 (2006)

Introduction: Thermo-electricity in molecular junction





Introduction: Thermo-electricity in molecular junction

Already heard about TE and its advantages (e.g. Shakuri) in this workshop.

Focus here: single-molecule junctions

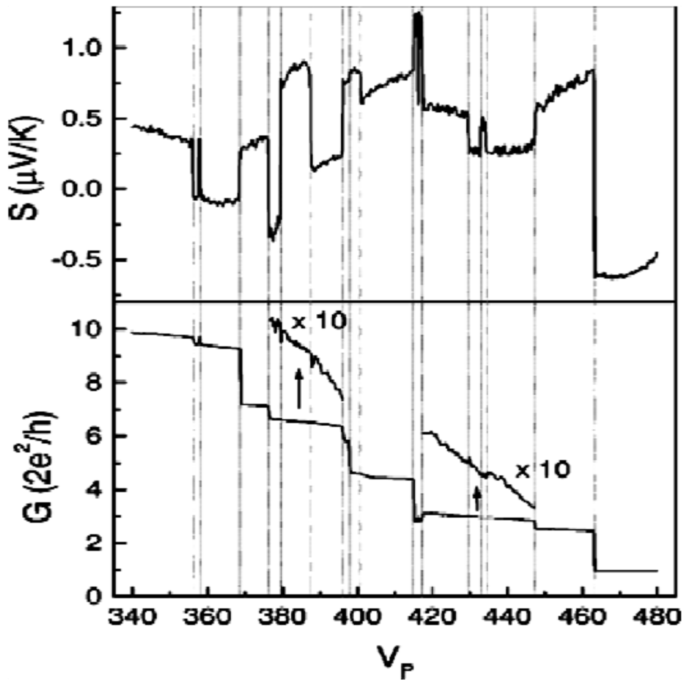
Motivation may already be understood:
(details will come later in theoretical part)

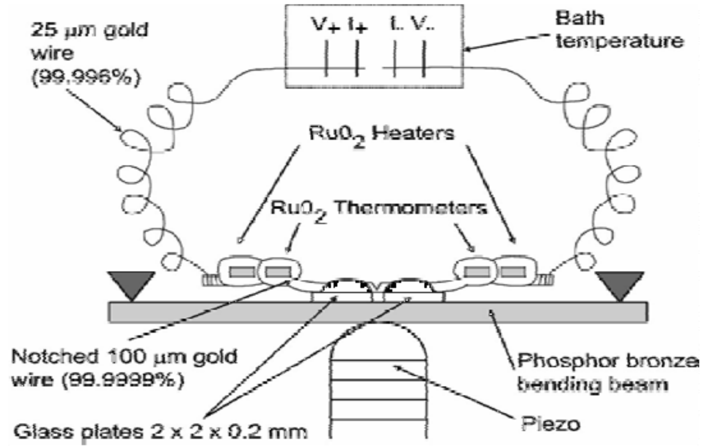
- Perfect miss-match for phonons= reduced thermal conductance
- Large “tunability” and “phase-space” (there are many molecules out there)

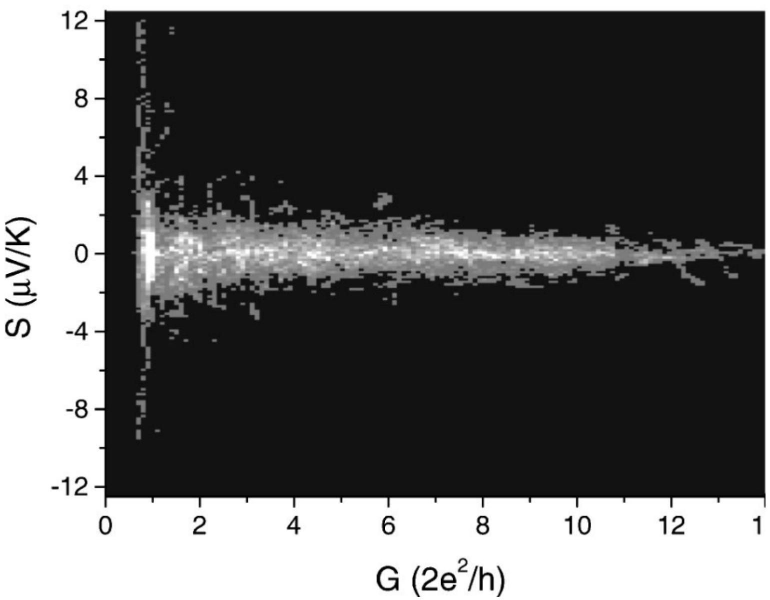
Atomic size metallic wires

Ludoph and Ruitenbeek,

Phys. Rev. B **59**, 12290 (1999)





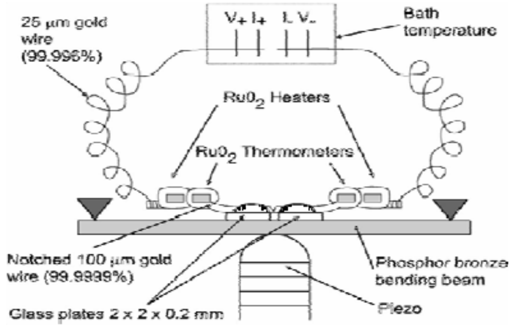


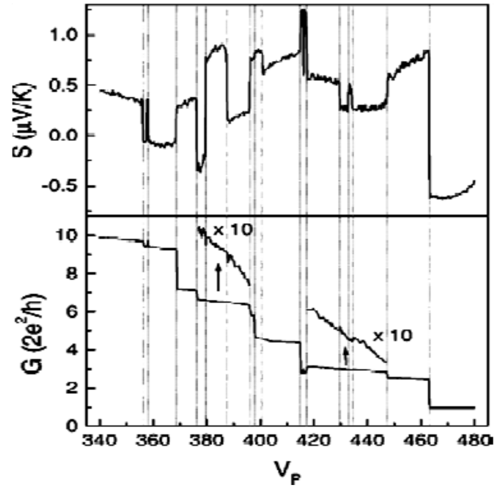
Introduction: Thermo-electricity in molecular junction

Atomic size metallic wires

[Ludoph and Ruitenbeek,

Phys. Rev. B **59**, 12290 (1999)]

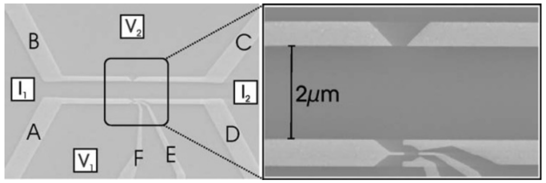


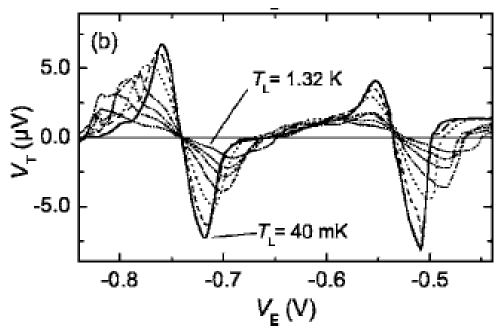


Quantum dots

[Scheibner *et al*,

Phys. Rev. B **75**, 041301(R) (2007)]

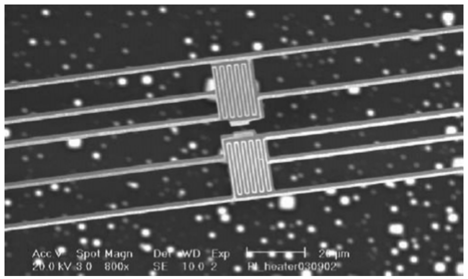


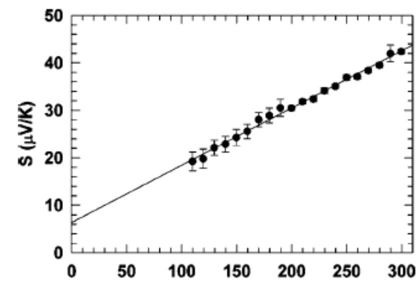


Carbon Nanotubes

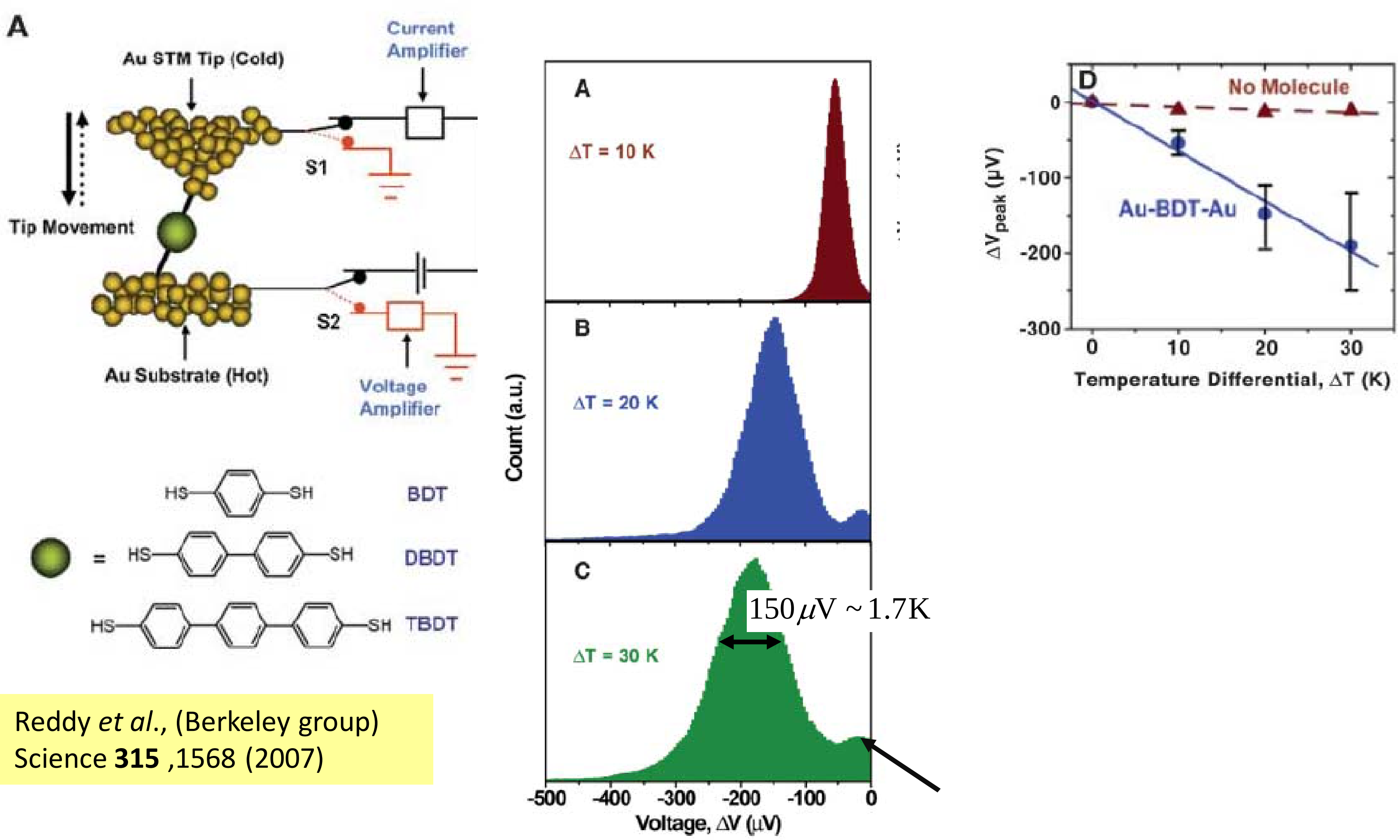
[Yu *et al*,

Nano Letters **5**, 1842 (2005)]



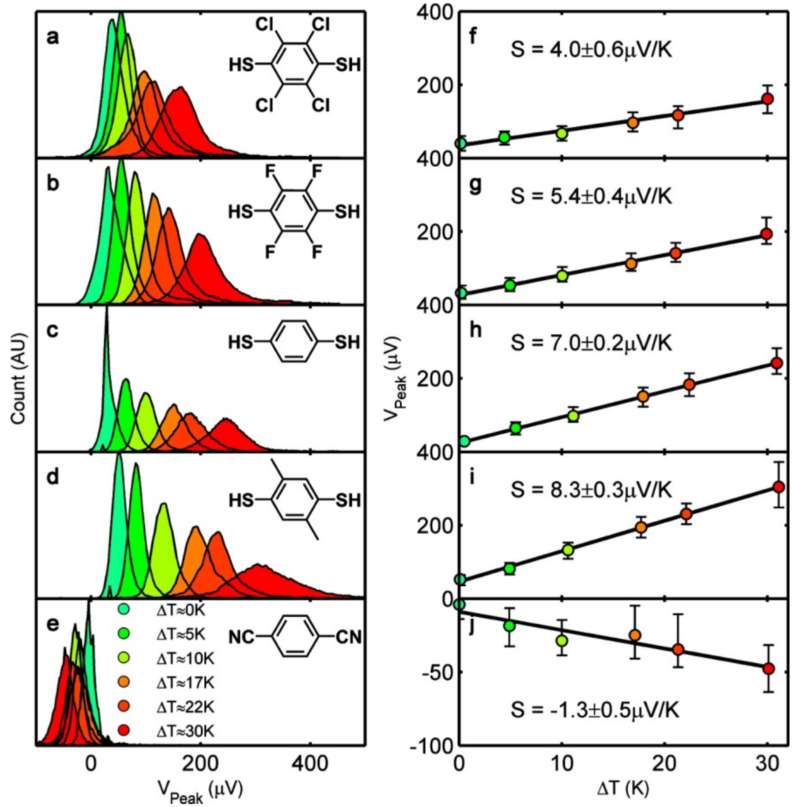


Introduction: Thermo-electricity in molecular junction



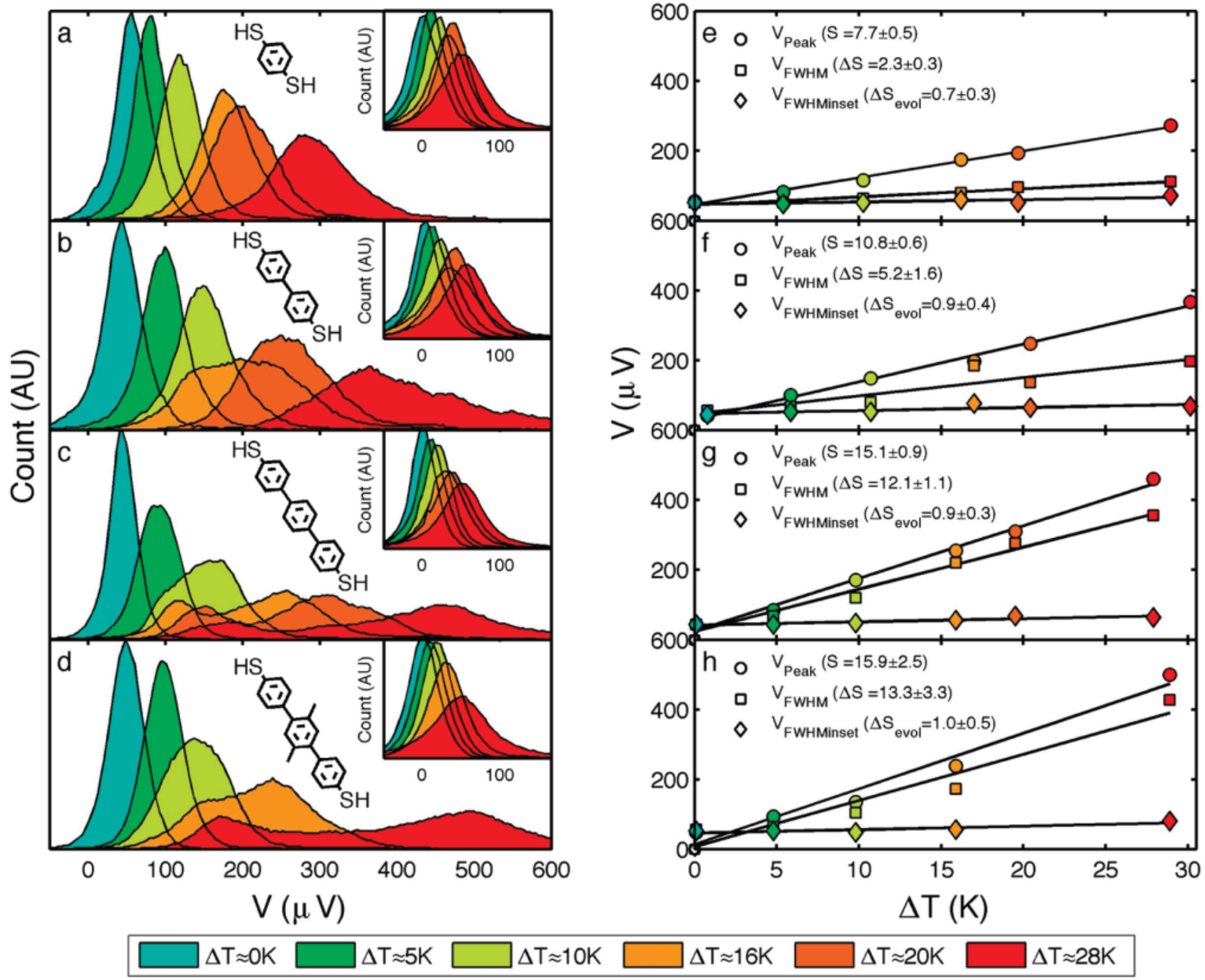
Reddy *et al.*, (Berkeley group)
Science **315** ,1568 (2007)

Introduction: Thermo-electricity in molecular junction



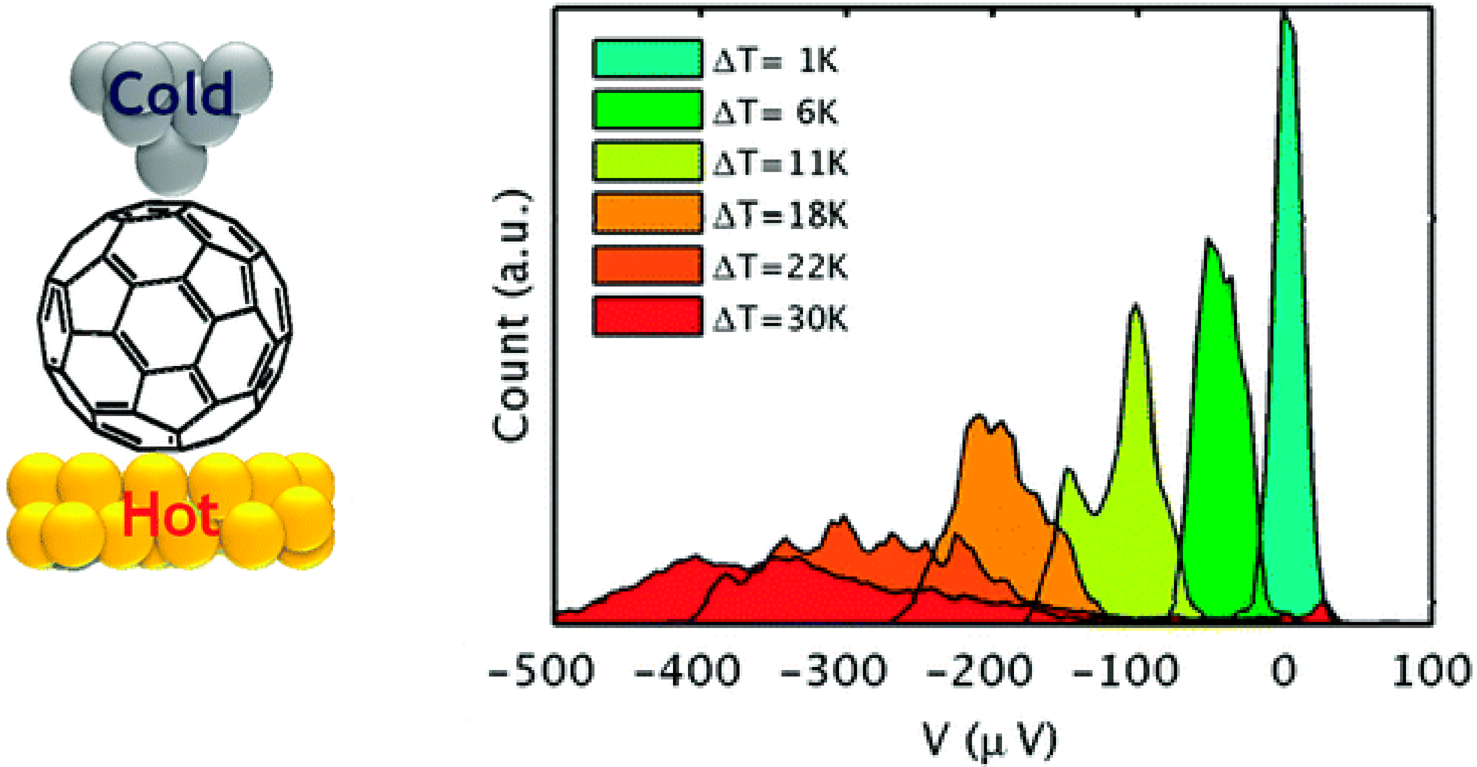
Baheti *et al*., Nano Lett. **8**, 715 (2008)

Introduction: Thermo-electricity in molecular junction

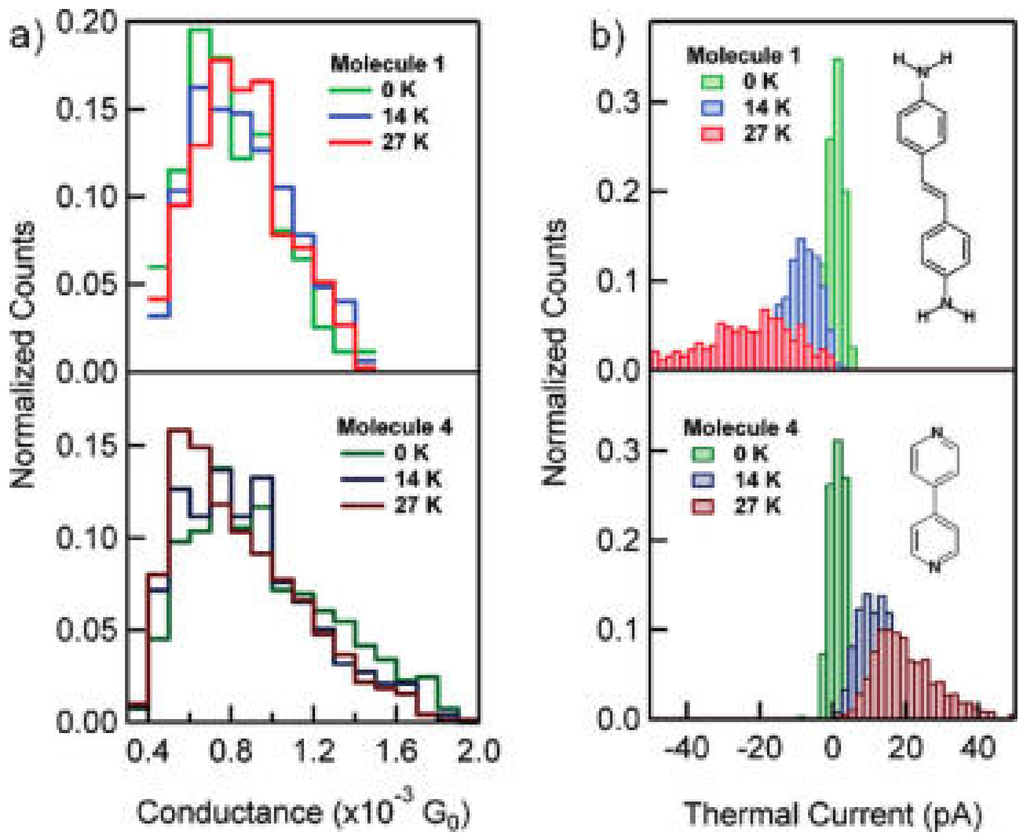


Malen *et al*., Nano Lett. **9**, 3406 (2009)

Introduction: Thermo-electricity in molecular junction

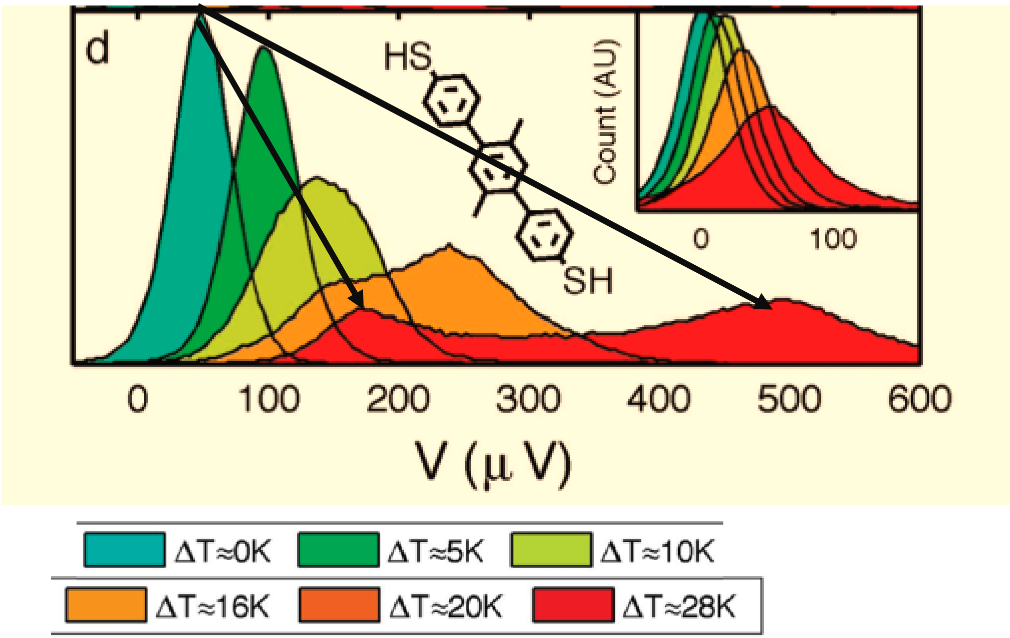


Yee *et al.*, Nano Lett.**11**, 4089 (2011)



Widawsky *et al*., Nano Lett.**12**, 354 (2012)

Introduction: Thermo-electricity in molecular junction



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

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

Intro summary:

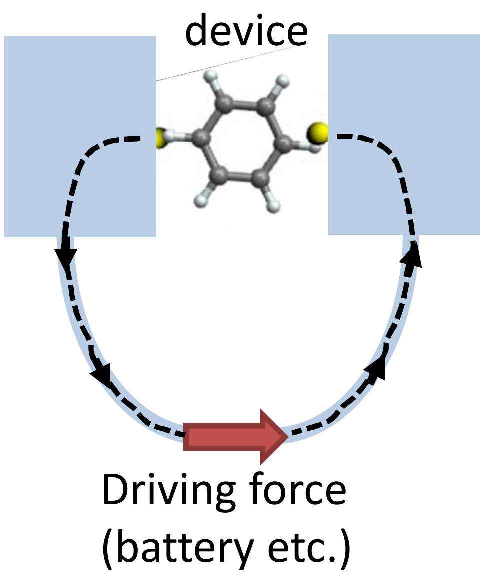
- Single-molecule thermopower measurements are possible
- Experiments always show strong variations in TE (and conductance)
- Eventually giving one number – the thermo-power *S*
- (but sometimes more than one number…)

Part II

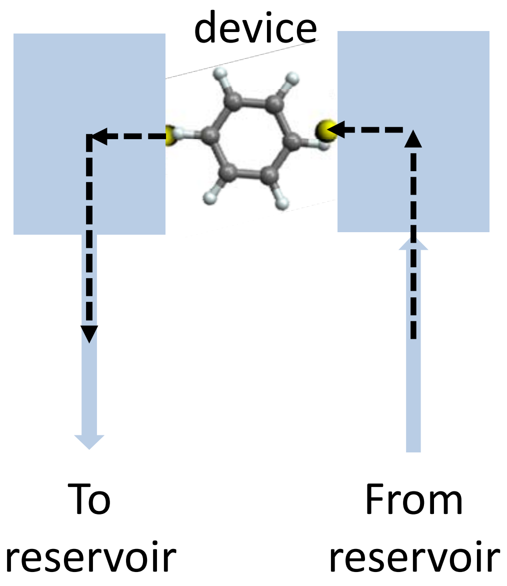
Theoretical description of energy transport in electronic molecular junctions

Basics of theoretical description of nano-junctions

Realistic systems: “closed circuit”



Model systems: “open circuit”



Open: easily modeled, but arbitrary approximations

Closed: better description of the experimental setups

Basics of theoretical description of nano-junctions – "Open circuits"

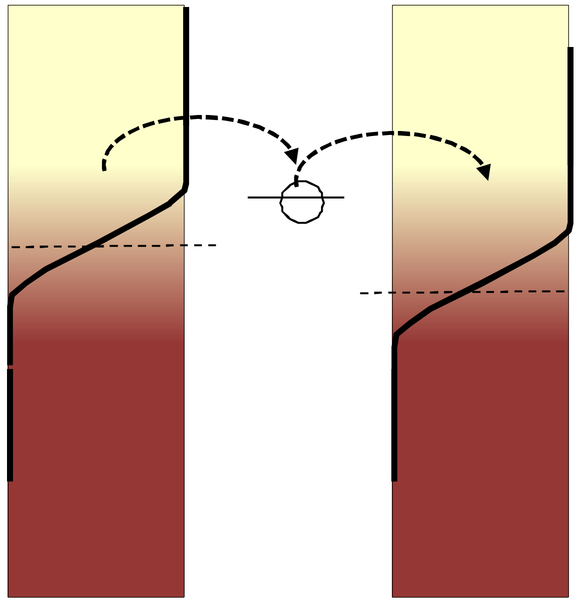
$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \mathcal{H}_M + \mathcal{H}_{L-M} + \mathcal{H}_{R-M}$$

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

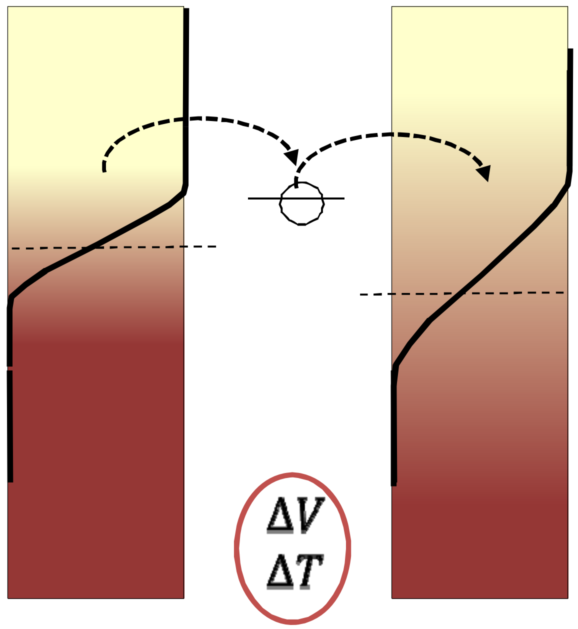
$$\mathcal{H}_R = \sum_k E_k\, c_{k,R}^\dagger c_{k,R}$$

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

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



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



At ΔT=0 we get: J=G ΔV

At J=0 we get:

$G\,\Delta V + GS\Delta T$=0 → S=- $\Delta V/\ \Delta T$

$$J_Q = GST\Delta V + (TGS^2 + \kappa)\Delta \mathrm{T}$$

$$= -TGS^2\Delta T + (TGS^2 + \kappa)\Delta \mathrm{T}$$

$$= \kappa\Delta \mathrm{T}$$

$$ZT = \frac{GS^2}{\kappa/T} \qquad \kappa = \kappa_e + \kappa_{ph} \qquad \eta = \frac{\eta_0\left(\sqrt{1+ZT}-1\right)}{\left(\sqrt{1+ZT}\right)+\frac{T_c}{T_H}}$$

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

At ΔT=0 we get: $J=G\,\Delta V$

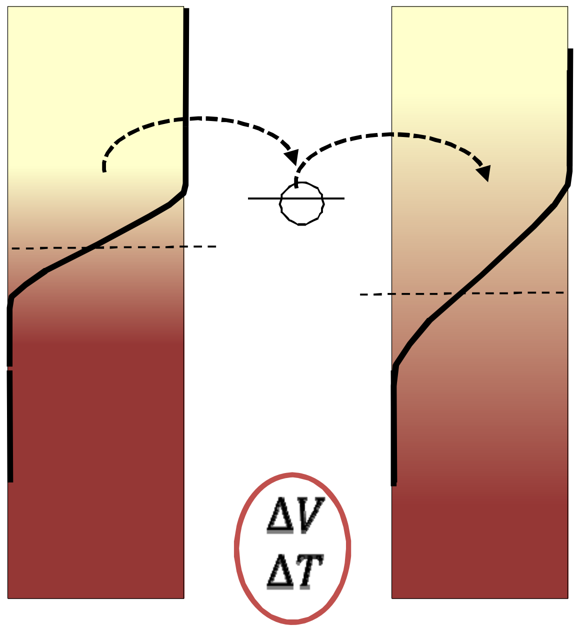
At J=0 we get:

$G\,\Delta V + GS\Delta T=0 \rightarrow S=-\,\Delta V/\,\Delta T$

$$J_Q = GST\Delta V + (TGS^2 + \kappa)\Delta \mathrm{T}$$

$$= -TGS^2\Delta T + (TGS^2 + \kappa)\Delta \mathrm{T}$$

$$= \kappa\Delta \mathrm{T}$$



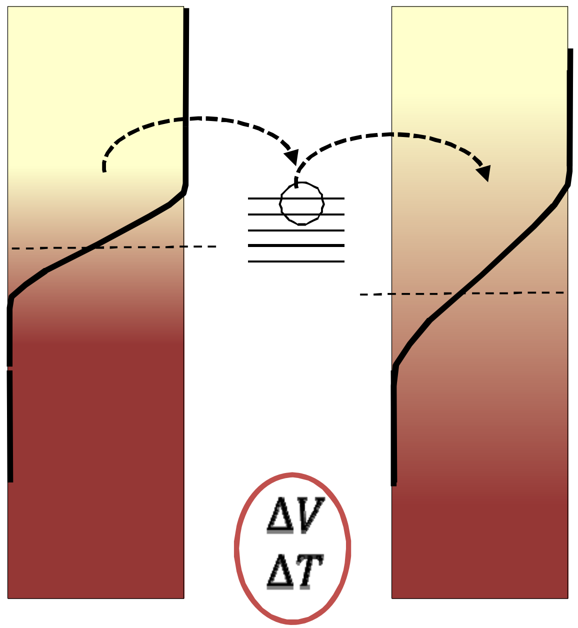
Different "methods" = different ways to calculate the currents

Part II.1

Theoretical description of energy transport in electronic molecular junctions:

Rate equations

Rate equations + Wide band limit:



- Is a "classical" calculation (no quantum interference)
- Electrodes DOS taken as constant
- Detailed balance is enforced

P_n - probability to find system in (Fock) state Ψ_n

Define the equation for P_n

$$P_n(t+dt) = P_n(t) + \Delta t \sum_{n'} (W_{n' \to n} P_{n'}(t) - W_{n \to n'} P_n(t))$$

Or

$$\frac{d}{dt} P_n(t) = \sum_{n'} (W_{n' \to n} P_{n'}(t) - W_{n \to n'} P_n(t))$$

$$\frac{d}{dt}P_n(t) = \sum_{n'}(W_{n'\to n}P_{n'}(t) - W_{n\to n'}P_n(t))$$

$$\frac{W_{n\to n'}}{W_{n'\to n}} = e^{-\Delta E_{nn'}}$$

Detailed balance

This doesn't include electron transfer to the electrodes:

This will generate additional terms

$$-\Gamma_{n,L}P_n + \Gamma'_{n,L}P_{n'}$$

$$\dot{P}_{n,L} = \gamma f_L(E_n)P_{n'} - \gamma(1 - f_L(E_n))P_n$$

- γ: Transfer rate
- $f_L(E_n)$: Probability to find an electron in the appropriate energy in the leads
- $P_{n'}$: State with one less electron than in Ψ_n
- $1 - f_L(E_n)$: Probability to find an empty state in the appropriate energy in the leads

Wide-band approximation:
$\gamma(E) = \gamma\,\delta(E - E_n)$
Electrons can tunnel into the molecule only with perfect energy matching

What is the current?

$$\dot{N} = J_L + J_R$$

Blackboard example: single molecular level, spin-less electrons

$$P_0, P_1 \qquad P_0 + P_1 = 1$$

$$J_L = \frac{\gamma L\ \gamma R\ \mathrm{Sech}\left[\frac{dV-2x}{2\,dT-4\,T}\right]\ \mathrm{Sech}\left[\frac{dV+2x}{2\,dT+4\,T}\right]\ \mathrm{Sinh}\left[\frac{2\,dV\ T-2\,dT\ x}{dT^2-4\,T^2}\right]}{2\,(\gamma L+\gamma R)} \qquad x = E_0 - \mu$$

$$G = \frac{1}{4\mathrm{T}}\frac{\gamma_L\gamma_R}{\gamma_{L+}\gamma_R}\mathrm{sech}\left(\frac{\mathrm{E}_0-\mu}{2\mathrm{T}}\right)^2$$

$$S = -\frac{E_0-\mu}{T}$$

What about the thermal conductance?

Same way:

$$\langle \dot{E} \rangle = J_{Q,L} - J_{Q,R}$$

For the single-electron molecule

we have $\dot{E} = (E_0 - \mu)\, P_1$, so for

this case $J_Q = (E_0 - \mu)J$

This gives $$\kappa = \frac{(1+T)x^2 \gamma L \gamma R \,\mathrm{Sech}[\frac{x}{2T}]^2}{4T^2(\gamma L + \gamma R)}$$

Exercise: Calculate ZT (answer might surprise you…)

A Letters Journal Exploring the Frontiers of Physics
March 2009
EPL, **85** (2009) 60010
doi: 10.1209/0295-5075/85/60010
www.epljournal.org

Thermoelectric efficiency at maximum power in a quantum dot

M. Esposito[1,2(a)], K. Lindenberg[1] and C. Van den Broeck[3]

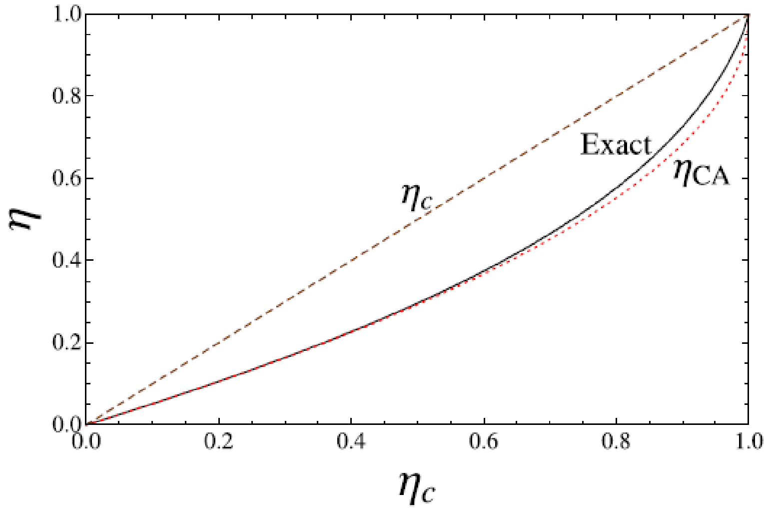
Curzon-Ahlborn efficiency

$$\eta_{CA} = 1 - \sqrt{1-\eta_C} \approx \frac{\eta_C}{2} + \frac{\eta_C^2}{8} + \frac{6\eta_C^3}{96} + \cdots$$

$$\dot{\mathcal{Q}}_r = (\varepsilon - \mu_r)\mathcal{I}_r = \alpha T_r x_r (f_r - f_l),$$

$$\dot{\mathcal{W}} = (\mu_l - \mu_r)\mathcal{I}_r = \alpha T_r \big(x_r - (1-\eta_c)x_l\big)(f_r - f_l)$$

$$x_\nu = \frac{\varepsilon - \mu_\nu}{T_\nu}, \qquad \nu = l, r.$$



$$\eta = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + \frac{[7 + \mathrm{csch}^2(a_0/2)]}{96}\eta_c^3 + \mathcal{O}(\eta_c^4)$$

More complicated example: molecular level with spin and Coulomb blockade:

$$P_0 \,, \qquad E_0 = 0$$

$$P_\uparrow \,, \qquad E_\uparrow = E_d$$

$$P_\downarrow \,, \qquad E_\downarrow = E_d$$

$$P_2 \,, \qquad E_0 = 2E_d + U$$

$$\dot{P}_0 = W_{\uparrow\to 0}\, P_\uparrow + W_{\downarrow\to 0}\, P_\downarrow - (W_{0\to\uparrow} + W_{0\to\downarrow})P_0$$

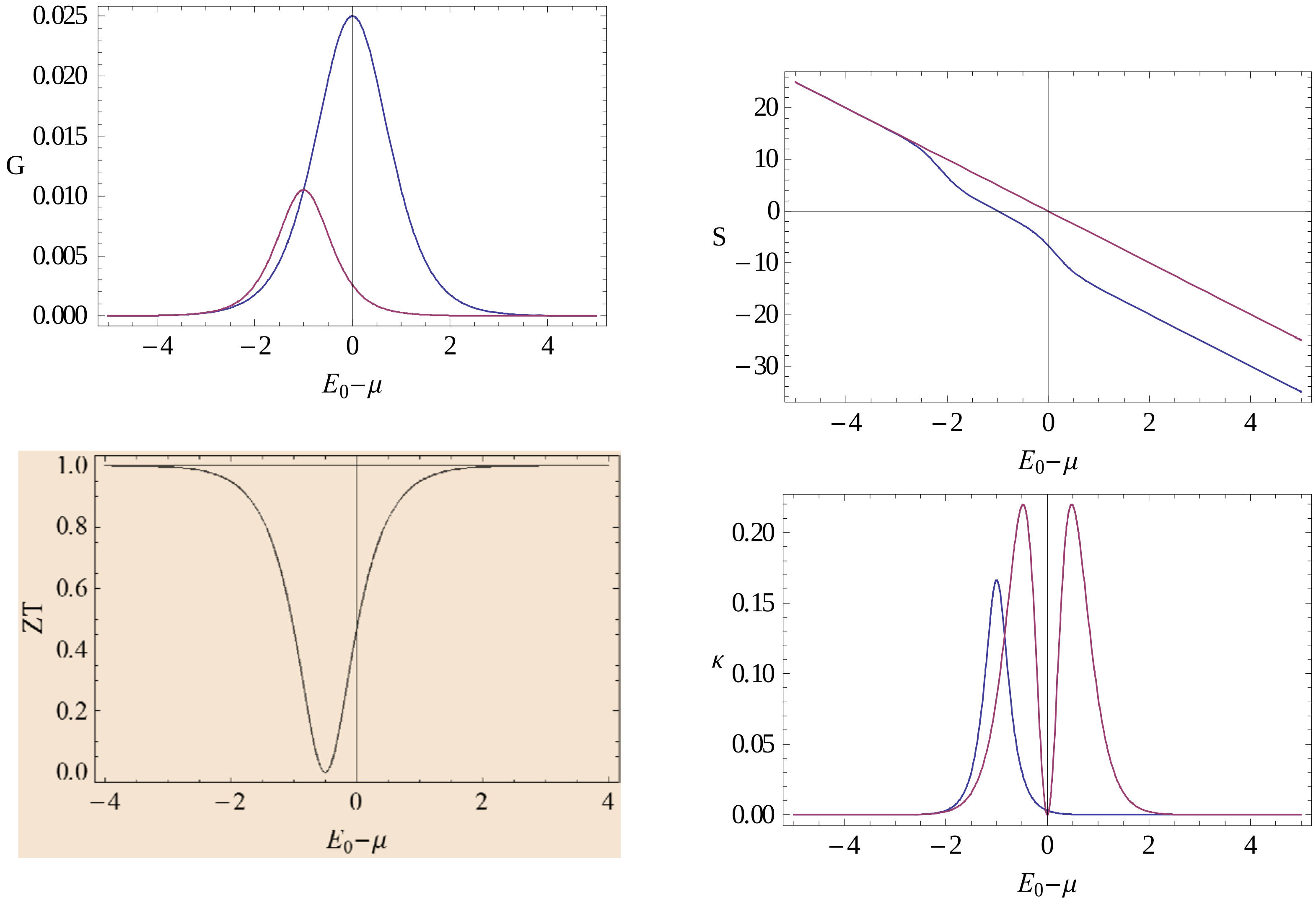
$$\dot{P}_\uparrow = W_{0\to\uparrow}P_0 + W_{2\to\uparrow}P_2 - (W_{\uparrow\to 0} + W_{\uparrow\to 2})P_\uparrow$$

$$\dot{P}_\downarrow = W_{0\to\downarrow}P_0 + W_{2\to\downarrow}P_2 - (W_{\downarrow\to 0} + W_{\downarrow\to 2})P_\uparrow$$

Beenakker and Staring,

Phys. Rev. B **46,** 9667 (1992)]

$T = 0.5, \gamma = 1, U = 2$



effect of phonon relaxation

Spin-less electrons

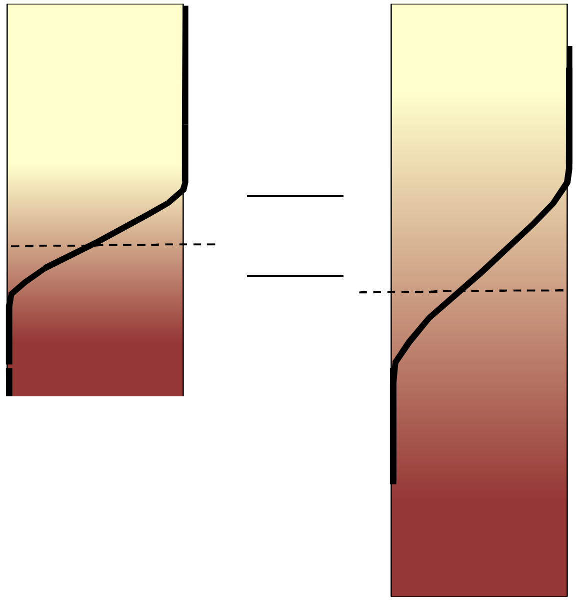
Two level molecule with very large U (double occupation prohibited)

$$P_0 \;, E = 0$$

$$P_1 \;, E = E_1$$

$$P_2 \;, E = E_2$$

$$P_{1+2} \;, E = E_1 + E_2 + U$$



PHYSICAL REVIEW B 70, 195107 (2004)

Thermopower of single-molecule devices

Jens Koch,[1] Felix von Oppen,[1] Yuval Oreg,[2] and Eran Sela[2]
[1]*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*
[2]*Department of Condensed Matter Physics, Weizmann Institute for Science, Rehovot 76100, Israel*
(Received 21 May 2004; published 12 November 2004)

Example: Thermo-spintronics: converting energy flow to spin-current

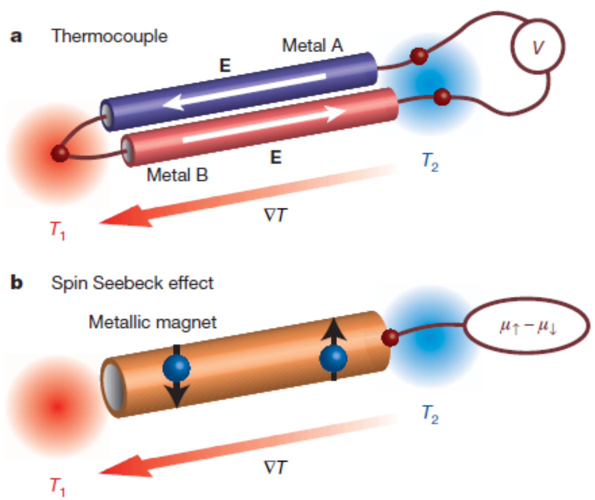
- Spintronics – Manipulating the electron spin (instead of charge)
- Reduced heat dissipation in spin-based elements
- Key Ingredient – Generating Spin-Voltage

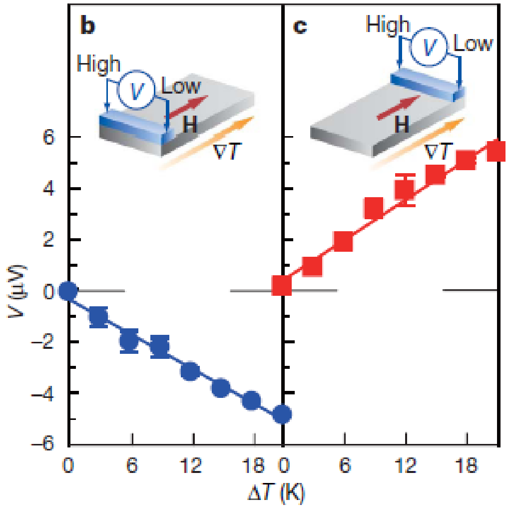
nature Vol 455 | 9 October 2008 | doi:10.1038/nature07321

LETTERS

Observation of the spin Seebeck effect

K. Uchida[1], S. Takahashi[2,3], K. Harii[1], J. Ieda[2,3], W. Koshibae[4], K. Ando[1], S. Maekawa[2,3] & E. Saitoh[1,5]



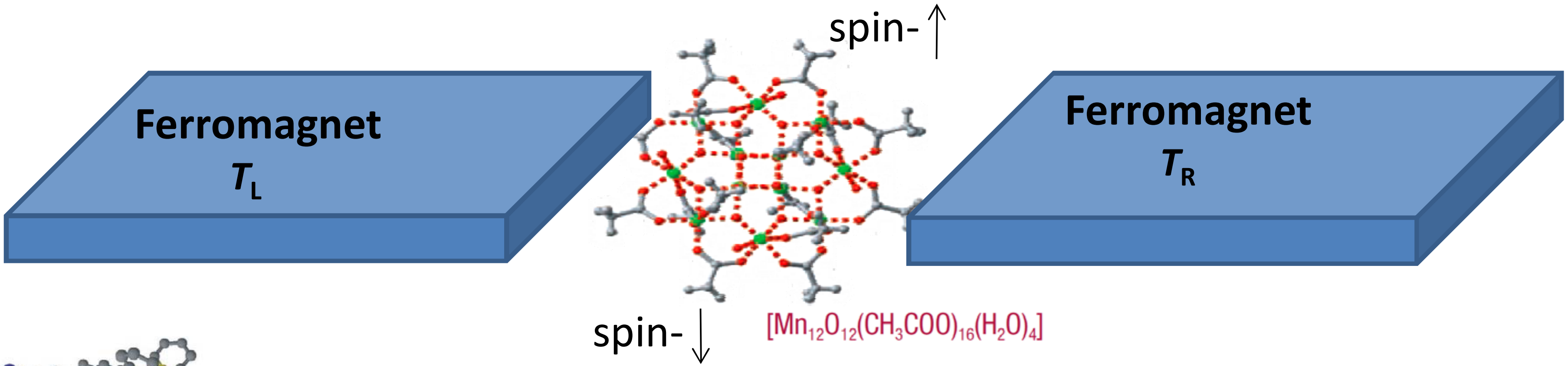


- Spin-thermopower very small
- Always accompanied by real current

Example: Thermo-spintronics: converting energy flow to spin-current

- Spin-thermopower very small
- Always accompanied by real current

Possible solution – A molecular (magnetic) junction between Ferromagnetic leads



$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$

$[Co(TerPy)_2]$

Divanadium $[(N,N',N''\text{-trimethyl-1,4,7-triazacyclononane})_2V_2(CN)_4(\mu\text{-}C_4N_4)]$

Dubi & Di Ventra, Phys. Rev. B **79**, 081302(R) (2009)

Example: Thermo-spintronics: converting energy flow to spin-current

- Spin-thermopower very small
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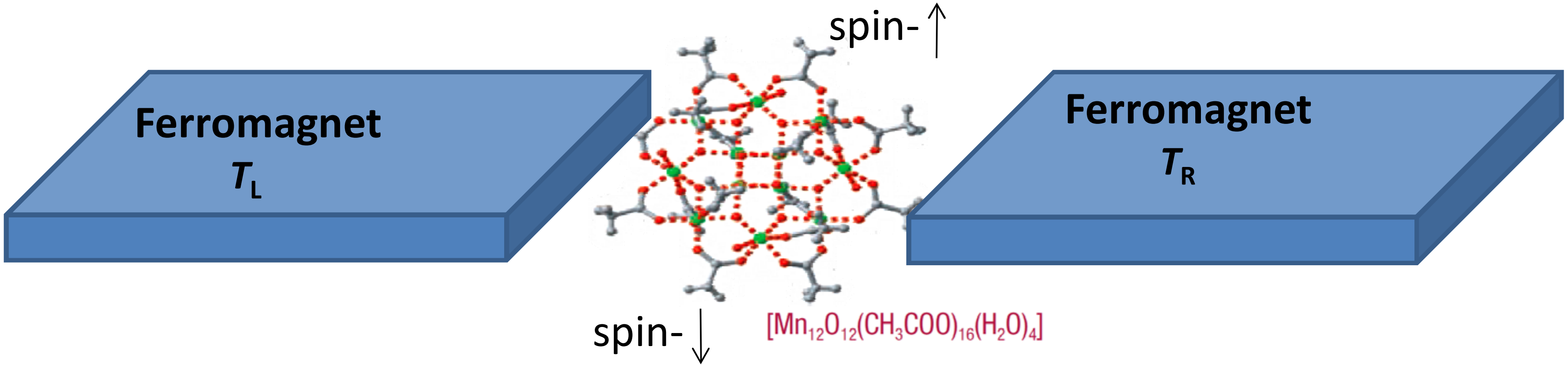


For this problem – **sequential tunneling rate equations** method

$$\frac{d}{dt}\begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \end{pmatrix} = \begin{pmatrix} -W_{0\to1}-W_{0\to2} & W_{1\to0} & W_{2\to0} & 0 \\ W_{0\to1} & -W_{1\to3}-W_{1\to0} & 0 & W_{3\to1} \\ W_{0\to2} & 0 & -W_{2\to3}-W_{2\to0} & W_{3\to2} \\ 0 & W_{1\to3} & W_{2\to3} & -W_{3\to1}-W_{3\to1} \end{pmatrix}\begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \end{pmatrix}$$

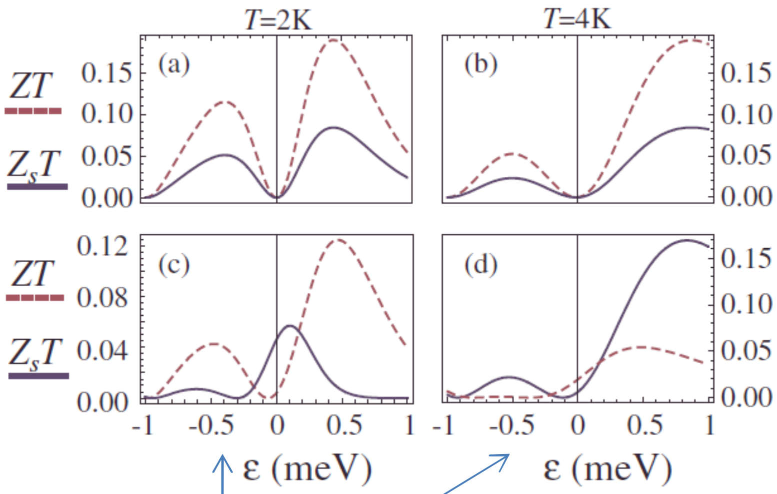
$$I_\nu = P_0(W^{(\nu)}_{0\to1} + W^{(\nu)}_{0\to2}) - P_1(W^{(\nu)}_{1\to0} - W^{(\nu)}_{1\to3}) - P_2(W^{(\nu)}_{2\to0} - W^{(\nu)}_{2\to3}) - P_3(W^{(\nu)}_{3\to1} + W^{(\nu)}_{3\to2})$$

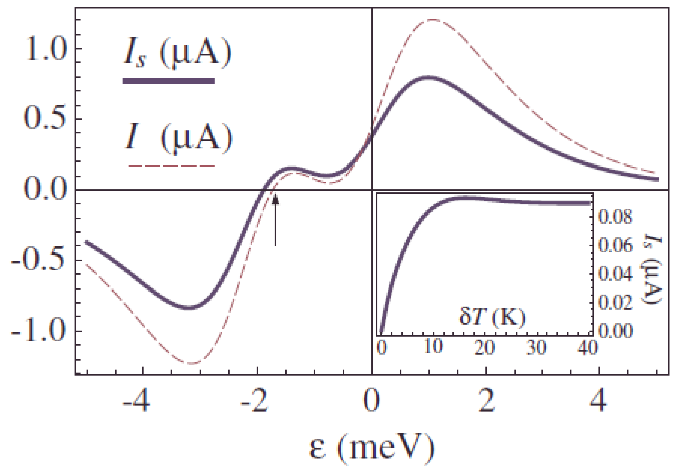
$$I_{s\nu} = P_0(W^{(\nu)}_{0\to1} - W^{(\nu)}_{0\to2}) - P_1(W^{(\nu)}_{1\to0} + W^{(\nu)}_{1\to3}) - P_2(W^{(\nu)}_{2\to0} + W^{(\nu)}_{2\to3}) - P_3(W^{(\nu)}_{3\to1} - W^{(\nu)}_{3\to2})$$

Example: Thermo-spintronics: converting energy flow to spin-current

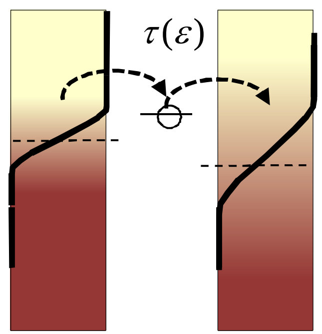
- Spin-thermopower very small
- Always accompanied by real current

Possible solution – A molecular (magnetic) junction between Ferromagnetic leads





Magnetic molecule



Dubi & Di Ventra, Phys. Rev. B **79**, 081302(R) (2009)

Example: Thermo-spintronics: converting energy flow to spin-current

- Spin-thermopower very small
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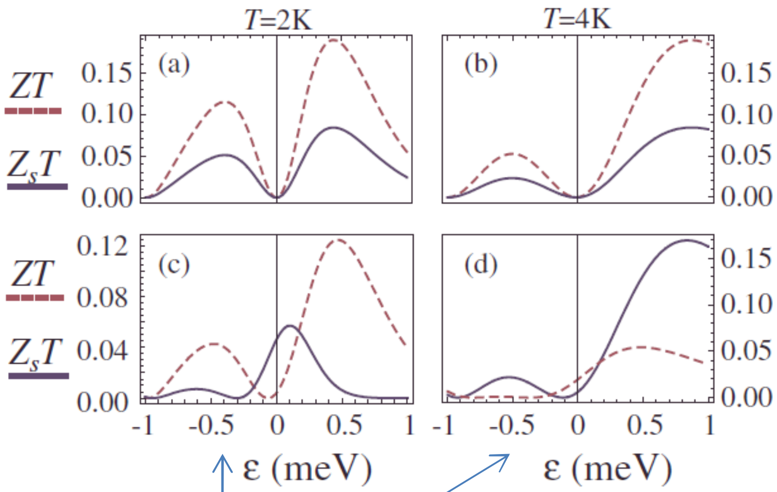
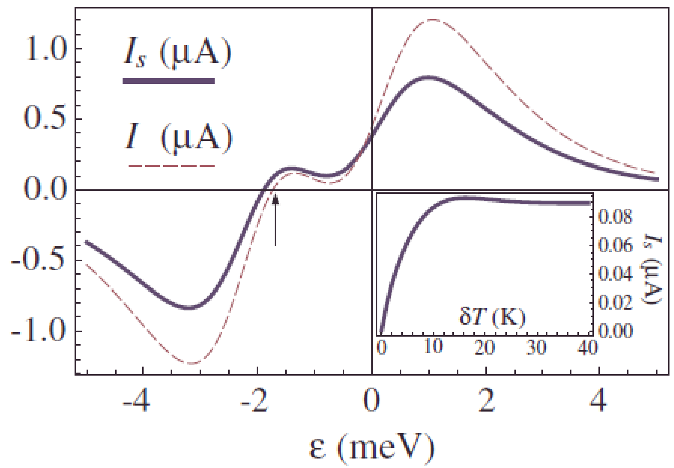
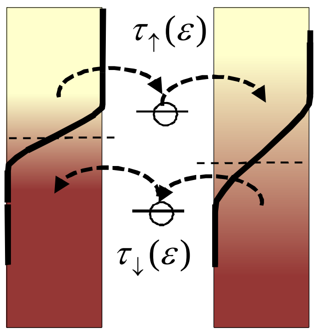




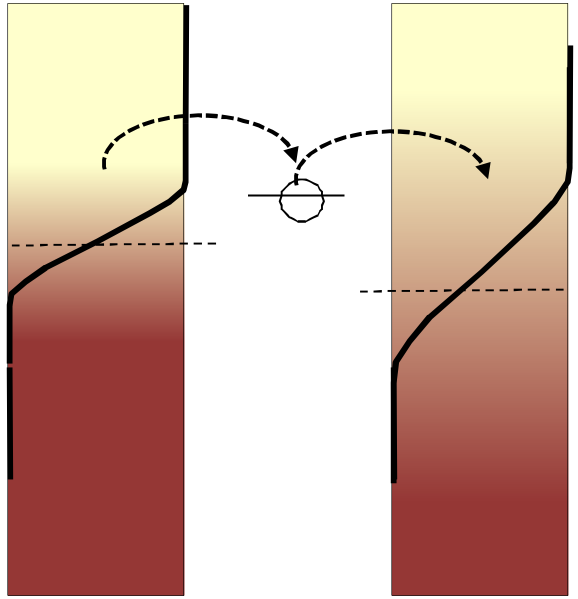
Magnetic molecule



Dubi & Di Ventra, Phys. Rev. B **79**, 081302(R) (2009)

From Rate equations to Landauer Formula:

$$J = \dot{N}_L$$
$$\dot{N}_L = -J_{in} + J_{out} = \cdots$$



We now resolve by energy :

$$P_{\rightarrow}(E) = \gamma(E) f_L(E)(1 - f_R(E))$$
$$P_{\leftarrow}(E) = \gamma(E) f_R(E)(1 - f_L(E))$$

And so

$$J = \int dE\, g(E)\gamma(E)[f_L(E)(1 - f_R(E)) - f_R(E)(1 - f_L(E))]$$
$$= \int dE\, g(E)\gamma(E)[f_L(E) - f_R(E)]$$

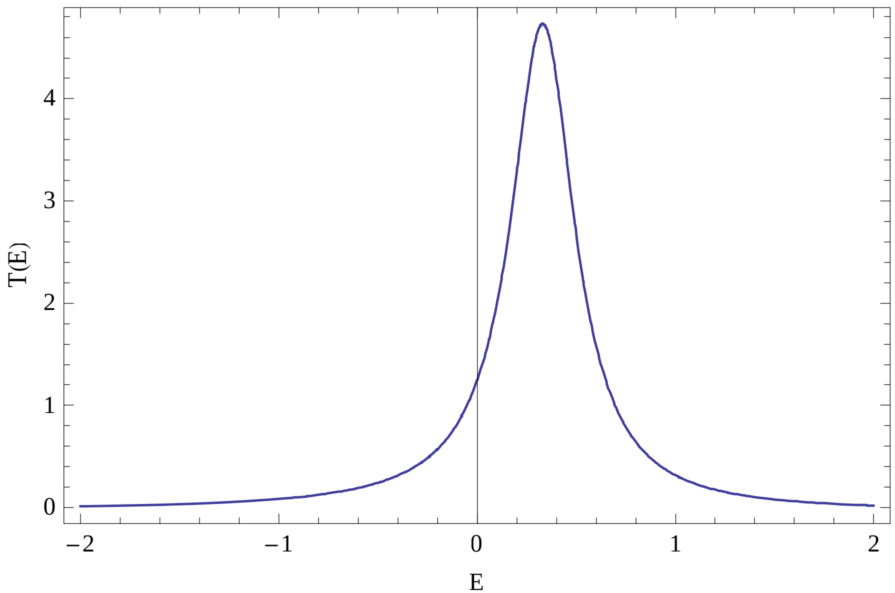
From Rate equations to Landauer Formula:

The Landauer-Buttiker formula

$$\gamma(E) = \frac{2e^2}{h}\left|t^\dagger t\right| = \frac{2e^2}{h} T(E)$$

Blackboard Example: linear chain with obstacle:

$$T(E) = \frac{v_1^2\left(1 + v_1\left(2 - Ek^2 + v_1\right)\right)}{(E0 - Ek)^2 + 2\,(E0 - Ek)\,Ek\,v_1^2 + 4\,v_1^4}$$



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)

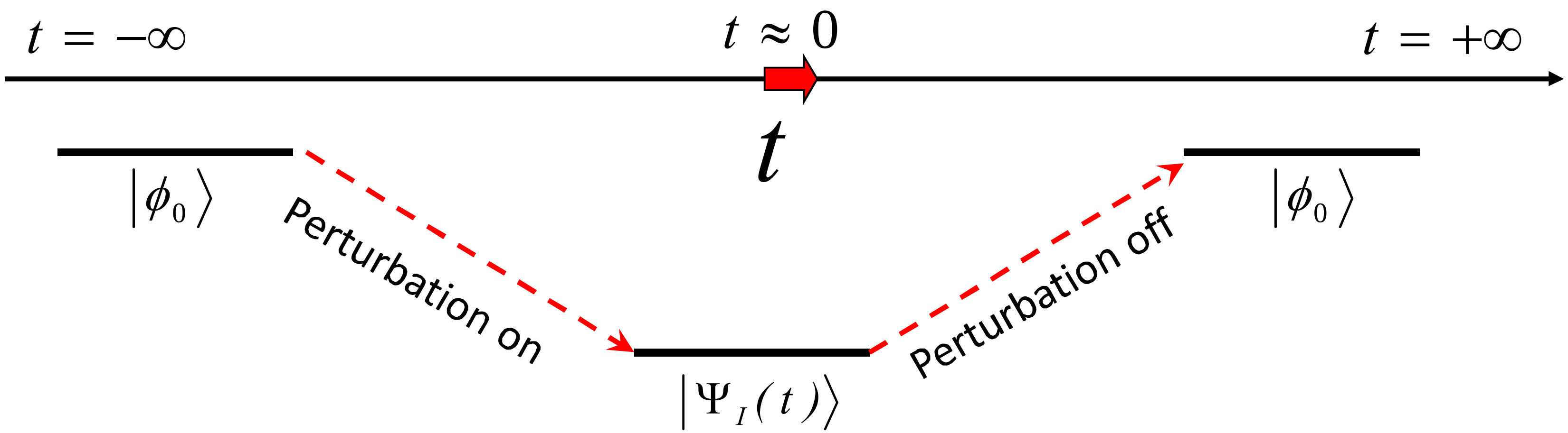
Two "intuitive" Green's functions:

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

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

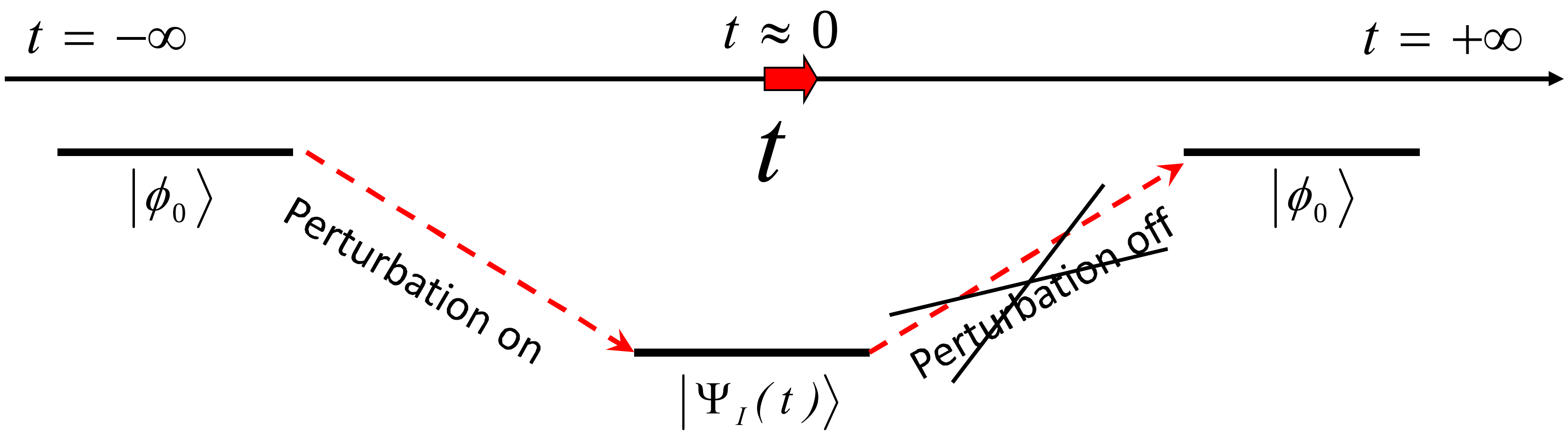
Lets remember the retarded Green's function formalism

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



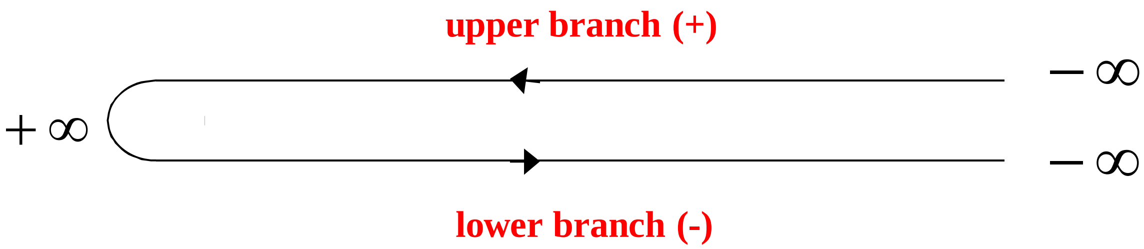
$$\langle \mathbf{A}(t) \rangle = \frac{\langle \phi_0 | \mathbf{S}(-\infty, t) \mathbf{A}_I(t) \mathbf{S}(t, -\infty) | \phi_0 \rangle}{\langle \phi_0 | \mathbf{S}(-\infty, t) \mathbf{S}(t, -\infty) | \phi_0 \rangle}$$

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



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

Keldysh's formal solution: a branched time-contour



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

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

equilibrium ***Keldish***

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:

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

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

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:

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

So what does this have to do with transport ?

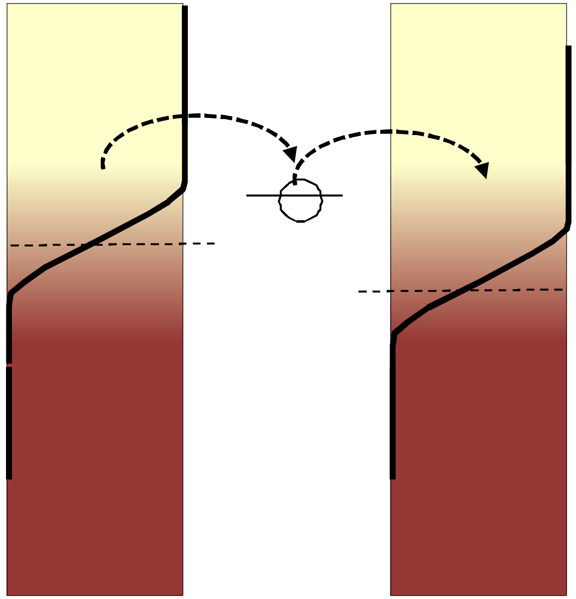
$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \mathcal{H}_M + \mathcal{H}_{L-M} + \mathcal{H}_{R-M}$$

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

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

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

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



VOLUME 68, NUMBER 16 PHYSICAL REVIEW LETTERS 20 APRIL 1992

Landauer Formula for the Current through an Interacting Electron Region

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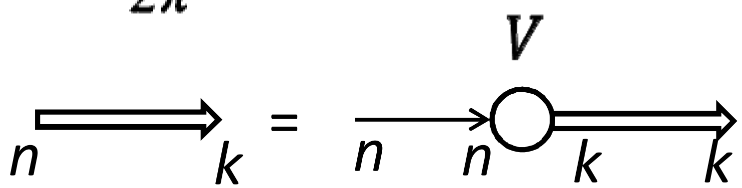
Ned S. Wingreen[(a)]
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 21 January 1992)

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

$$J = \frac{ie}{\hbar} \sum_{\substack{k,\alpha \in L \\ n}} \left(V_{k\alpha,n} \langle \mathbf{c}^\dagger_{k\alpha} \mathbf{d}_n \rangle - V^*_{k\alpha,n} \langle \mathbf{d}^\dagger_n \mathbf{c}_{k\alpha} \rangle \right)$$

$$= \frac{e}{\hbar} \sum_{\substack{k,\alpha \in L \\ n}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left[V_{k\alpha,n} G^<_{n,k\alpha}(\omega) - V^*_{k\alpha,n} G^<_{k\alpha,n}(\omega) \right]$$



$$J = \frac{ie}{2h} \int d\epsilon \Big(\mathrm{tr}\{[f_L(\epsilon)\Gamma^L - f_R(\epsilon)\Gamma^R](\mathbf{G}^r - \mathbf{G}^a)\} + \mathrm{tr}\{(\Gamma^L - \Gamma^R)\mathbf{G}^<\} \Big),$$

where $\Gamma^L_{n,m} = 2\pi \sum_{\alpha \in L} \rho_\alpha(\epsilon) V_{\alpha,n}(\epsilon) V^*_{\alpha,m}(\epsilon)$

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

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

And for the non-interacting system

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

Similarly

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

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

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

$$G = \frac{J}{\Delta V}\bigg|_{\Delta T=0} = e^2 L_0$$
$$S = \frac{\Delta V}{\Delta T}\bigg|_{J=0} = L_1/(eTL_0)$$
$$\kappa_e = \frac{J_Q}{\Delta T}\bigg|_{\mathrm{J}=0} = (L_2 - \frac{L_1^2}{L_0})/T$$

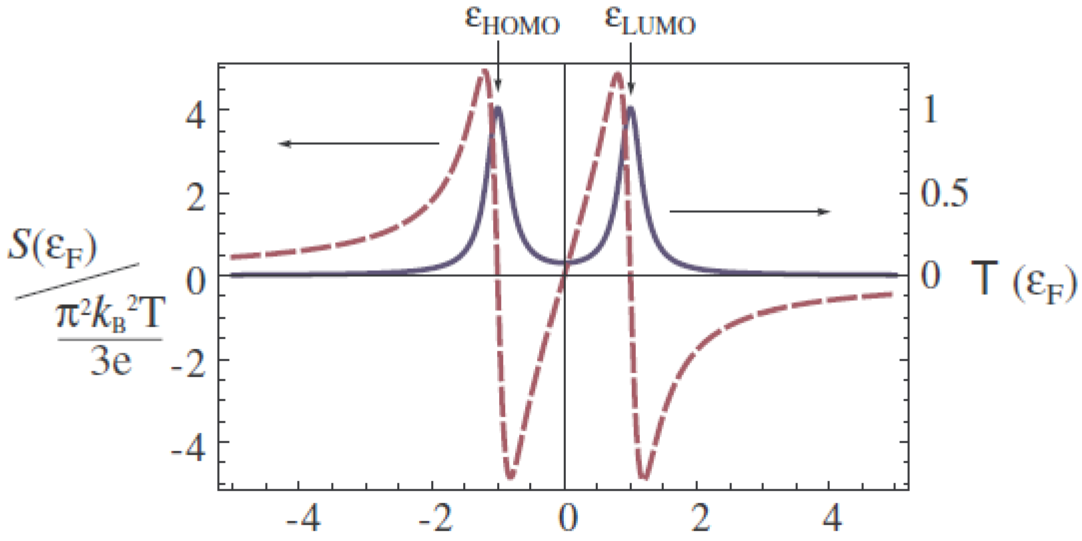
With

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

Low-temperature limit:

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

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



[redacted]

Key publications:

PHYSICAL REVIEW B **67**, 241403(R) (2003)

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
(Received 27 January 2003; published 26 June 2003)

PHYSICAL REVIEW B **72**, 165426 (2005)

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

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Department of Chemical Physics, Weizmann Institute of Science, 76100 Rehovot, Israel
(Received 20 April 2005; revised manuscript received 21 June 2005; published 26 October 2005)

PHYSICAL REVIEW B **78**, 161406(R) (2008)

Optimal thermoelectric figure of merit of a molecular junction

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

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

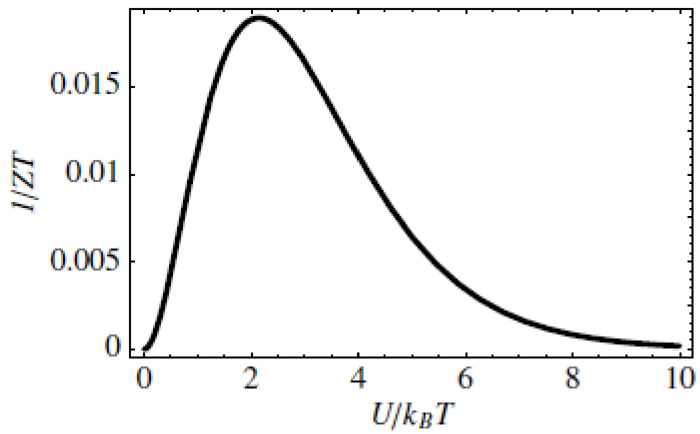
$$I_Q^{\mathrm{el}} = \frac{1}{h}\int_{-2t}^{2t} dE(E-\mu)[\mathcal{T}_\uparrow(E) + \mathcal{T}_\downarrow(E)][f_L^0(E) - f_R^0(E)].$$

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

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

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

$$ZT = \frac{1}{\bar{\gamma}}\frac{\pi\delta^2}{4\cosh^2(\delta/2)} + \mathcal{O}(\bar{\gamma}^0)$$



Intermediate Summary : The NEGF and the Landauer formula

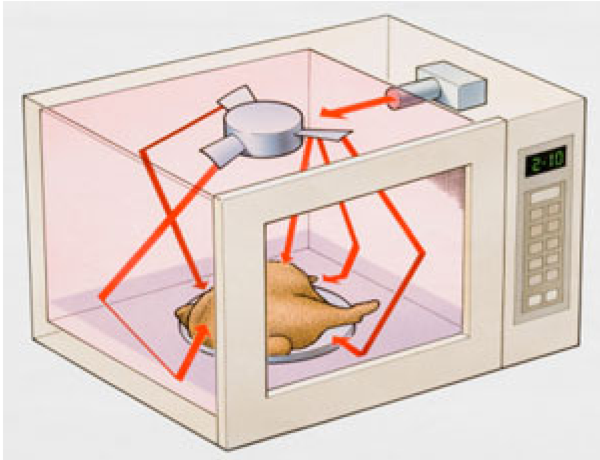
- straight-forward derivation
- "Easy" to implement

- 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

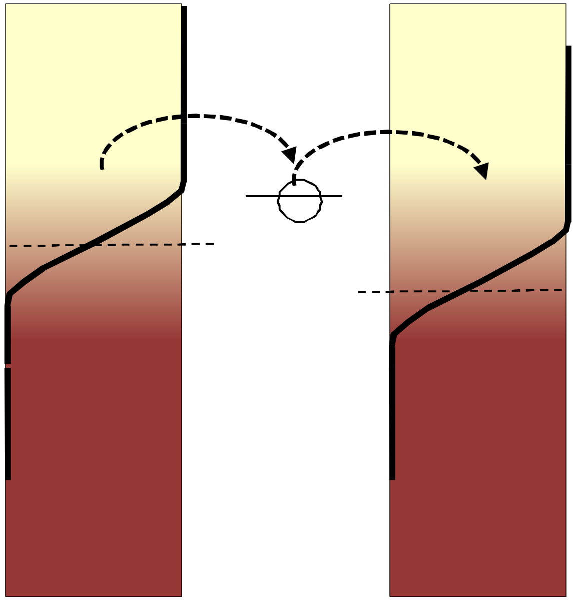
Microwave-mediated heat transport in a quantum dot attached to leads

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



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



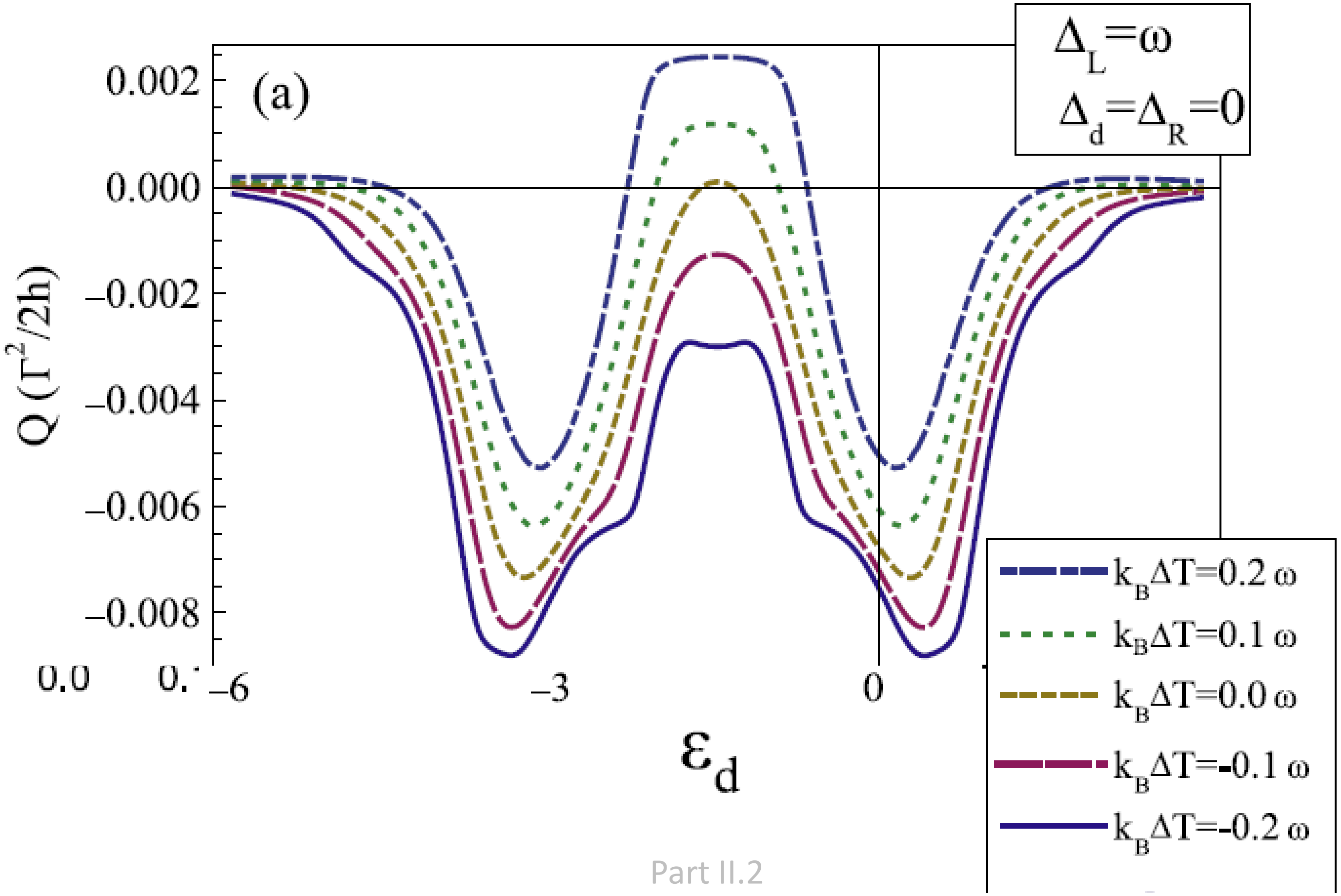
$$H(t) = \sum_{k,\sigma,\beta} \varepsilon_{k\beta}(t) c^\dagger_{k\beta\sigma} c_{k\beta\sigma} + \sum_\sigma \varepsilon_d(t) d^\dagger_\sigma d_\sigma + U d^\dagger_\uparrow d_\uparrow d^\dagger_\downarrow d_\downarrow + \sum_{k,\sigma,\beta} (V_{\beta d} c^\dagger_{k\beta\sigma} d_\sigma + \text{H.c.}),$$

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

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

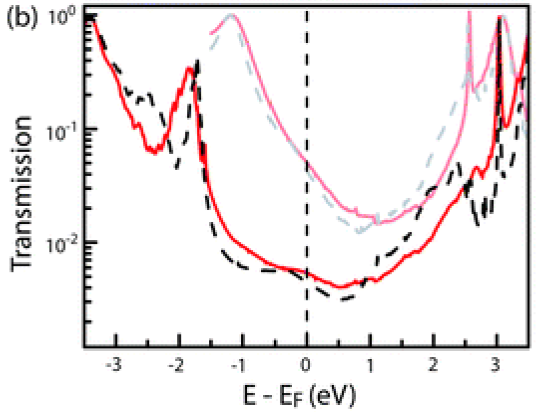
$$\begin{aligned} G^r_\sigma(t, t') = -\mathrm{i}\theta(t - t') \Big\{ &(1 - n_{\bar\sigma}) \\ &\times \exp\left(-\mathrm{i} \int_{t'}^{t} \varepsilon_d(\tau)\, \mathrm{d}\tau - \frac{\Gamma}{2}(1 - n_{\bar\sigma})(t - t') \right) \\ &+ n_{\bar\sigma} \exp\left(-\mathrm{i} \int_{t'}^{t} [\varepsilon_d(\tau) + U]\, \mathrm{d}\tau - \frac{\Gamma}{2} n_{\bar\sigma}(t - t') \right) \Big\} \end{aligned}$$

$$A_{\beta\sigma}(\varepsilon,t) = \sum_{k,k'} J_k(\frac{\Delta_d-\Delta_\beta}{\omega}) J_{k'}(\frac{\Delta_\beta-\Delta_d}{\omega}) e^{i(k+k')\omega t}$$
$$\times \{\frac{1-n_{\bar\sigma}}{\varepsilon-\varepsilon_d-k'\omega+i\Gamma(1-n_{\bar\sigma})/2} + \frac{n_{\bar\sigma}}{\varepsilon-\varepsilon_d-U-k'\omega+i\Gamma n_{\bar\sigma}/2}\}$$
$$= \sum_k J_k^2(\frac{\Delta_d-\Delta_\beta}{\omega})[\frac{1-n_{\bar\sigma}}{\varepsilon-\varepsilon_d-k\omega+i\Gamma(1-n_{\bar\sigma})/2} + \frac{n_{\bar\sigma}}{\varepsilon-\varepsilon_d-U-k\omega+i\Gamma n_{\bar\sigma}/2}].$$

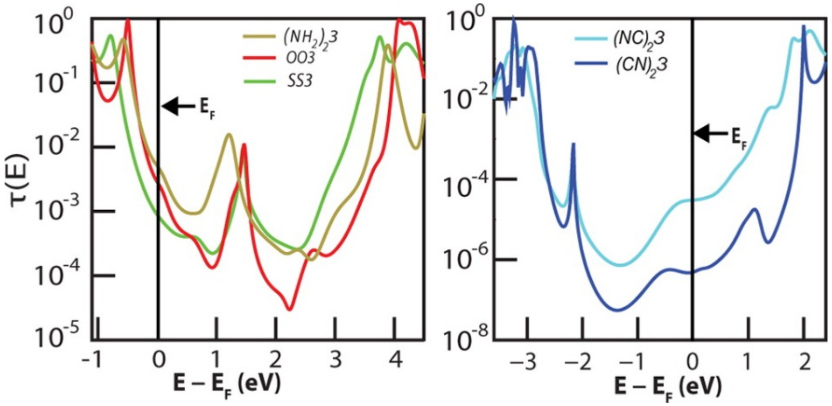


NEGF+DFT

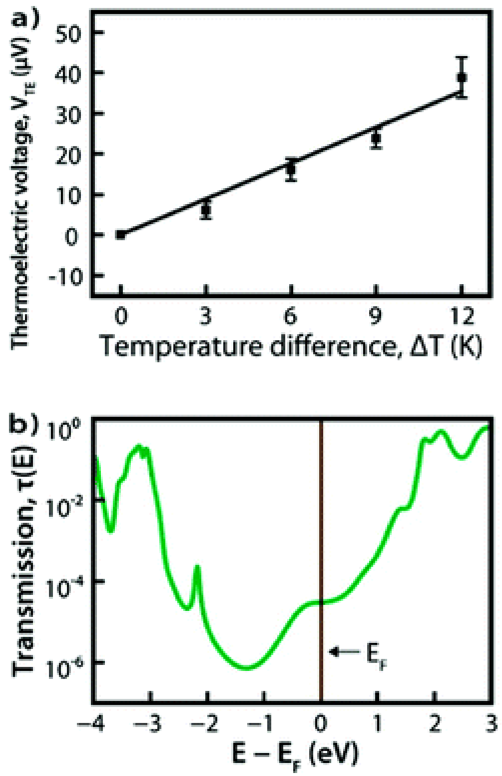
- Use DFT to calculate the Green's functions
- Use Green's function to calculate *T(E)* via Landauer formula *Use*
- *T(E)* to calculate thermopower



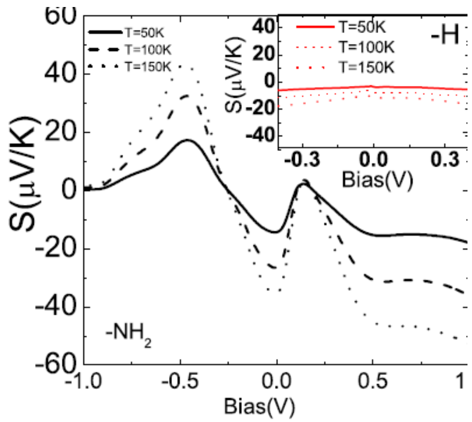
Quek et al
ACS Nano **2011** *5* (1), 551-55



Balachandran et al.,
The Journal of Physical Chemistry Letters **2012** *3* (15), 1962-1967

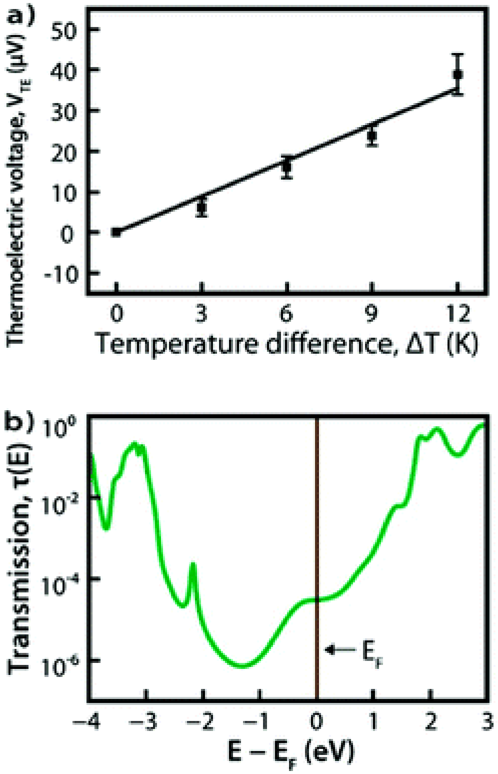


Tan et al.,
Journal of the American Chemical Society **2011** *133* (23), 8838-8841

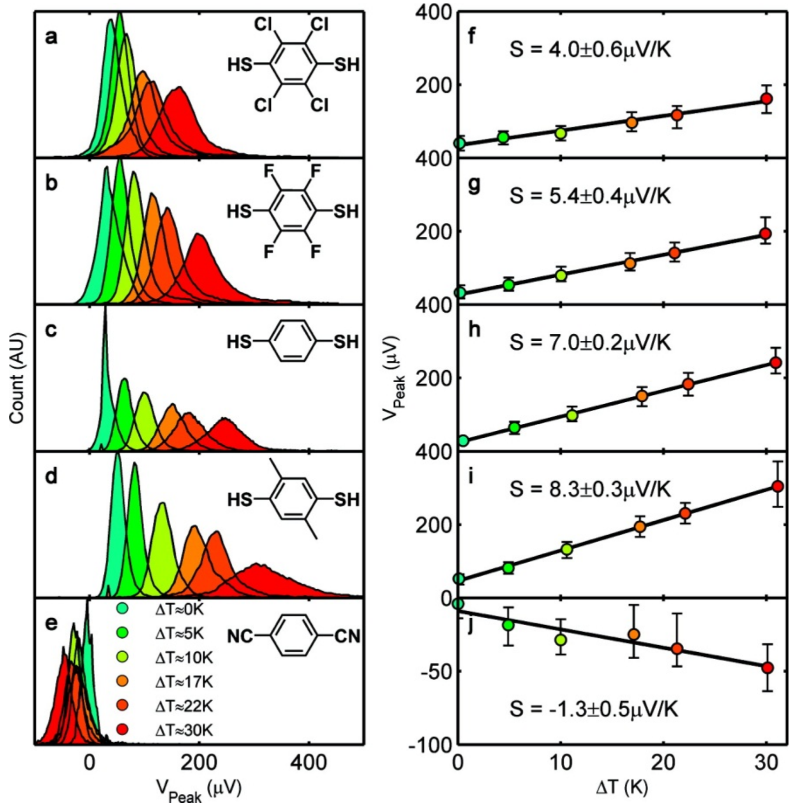


Liu and Chen
PRB **79**, 193101 (2009)

Does this:



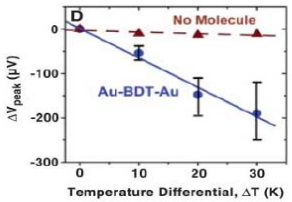
Explain this:

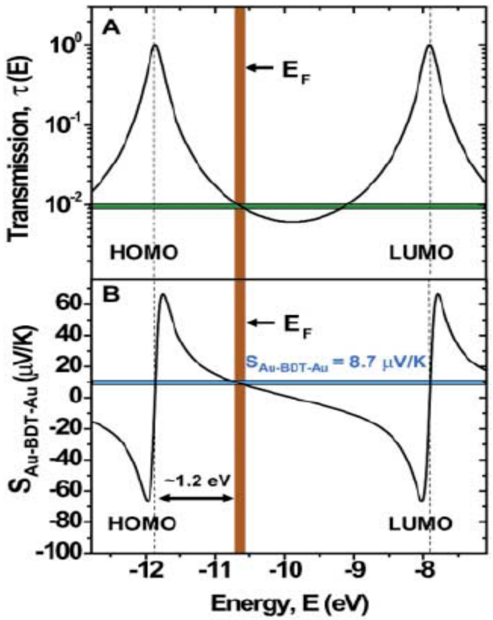


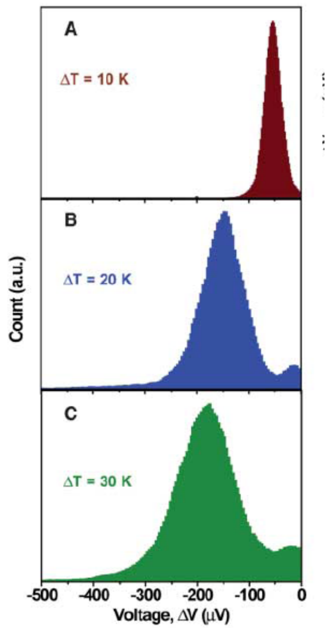
16 MARCH 2007 VOL 315 SCIENCE www.sciencemag.org

Thermoelectricity in Molecular Junctions

Pramod Reddy,[1*] Sung-Yeon Jang,[2,3*†] Rachel A. Segalman,[1,2,3‡] Arun Majumdar[1,3,4‡]

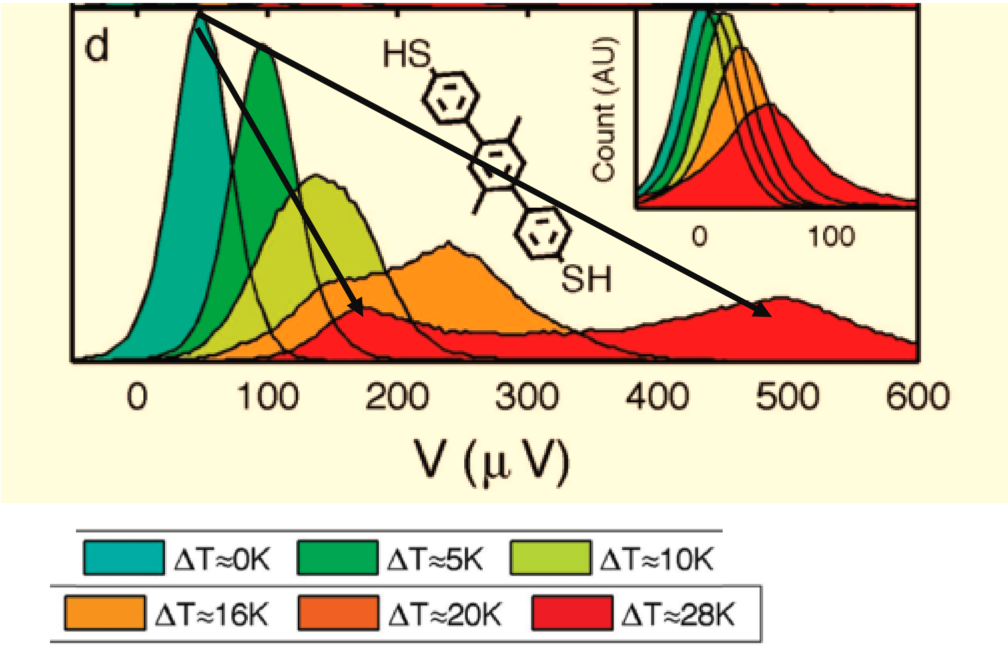






- Extremely impressive experiment !!
- Analysis based on Landauer Formula:
  - not at the low *T* limit
  - not necessarily in Linear response
  - Fluctuations not accounted for
  - Additional structure not explained

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?

$E_n \to E_n + \delta E$

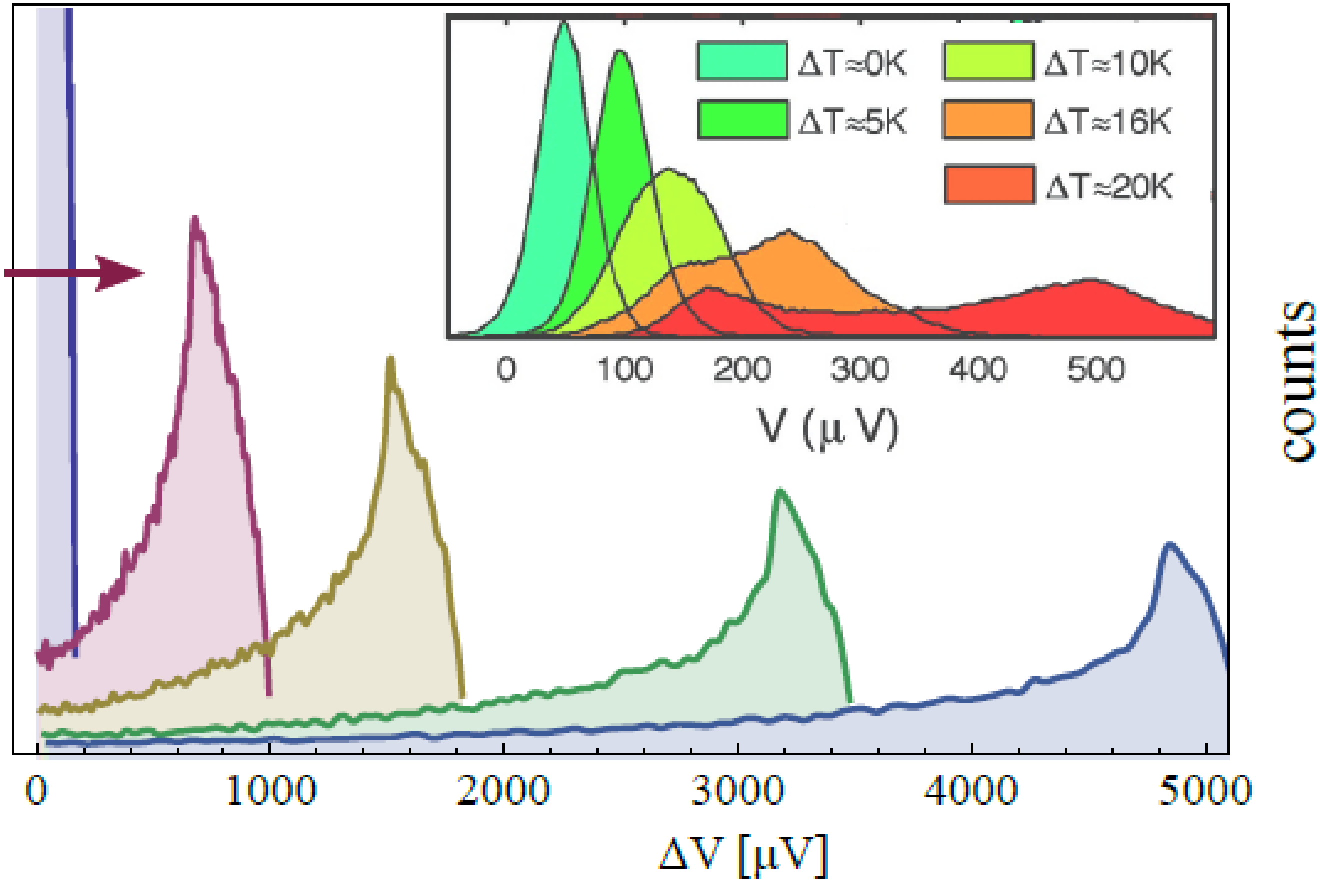
One finds:

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

Analysis of thermopower fluctuations with Landauer:

$$\frac{n - E_F)}{E_n - E_F)^2}$$

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

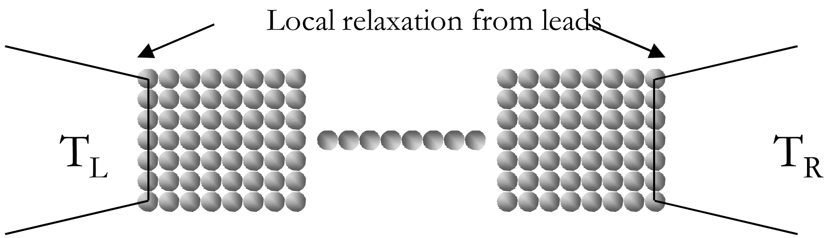
This equation :

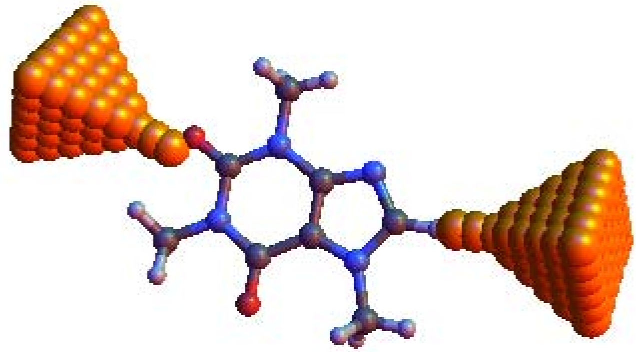
- Conserves norm *on average*
- Hamiltonian and *V*-operators can be interacting and time-dependent

An open Quantum System Approach

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





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:

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

Hamiltonian term

Relaxation term (environment)

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

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

- Environment taken in the Markov approximation
- 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:

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

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

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

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

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

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

Need to be determined

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

We need to :

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

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

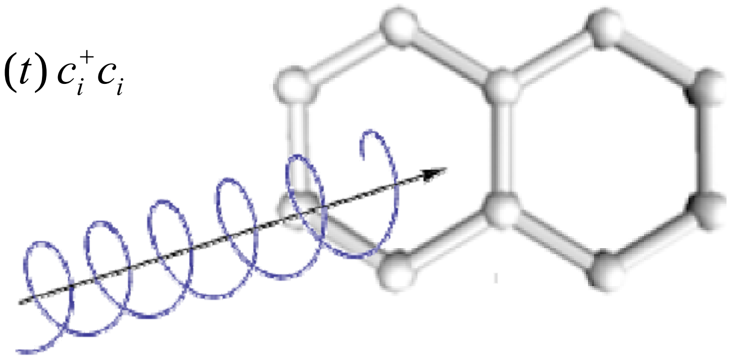
Comparison between full Many-Body and Single-Particle equations:

Example 1 – driven system at T=0

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

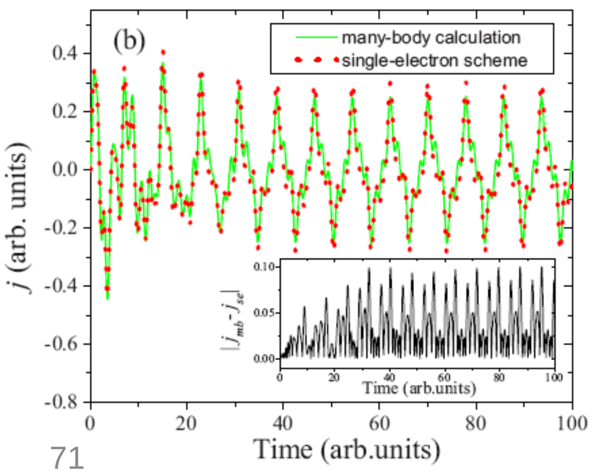
$$\mathbf{E} = E_0(\mathbf{x}\cos(\omega t) + \mathbf{y}\sin(\omega t))$$

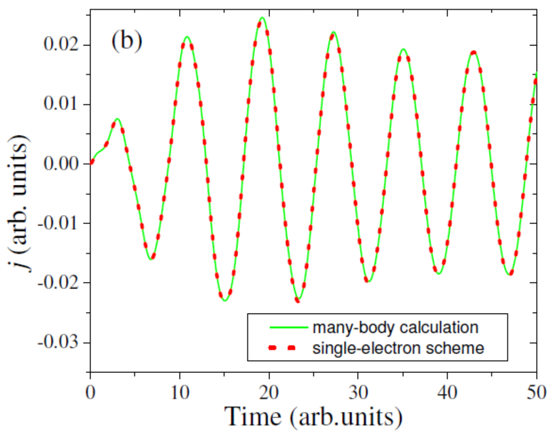
$$V_{kk'}^{(i)} = \sqrt{\gamma\, f_D(\varepsilon_k)}\,\delta_{ik}(1-\delta_{kk'})\left|k\right\rangle\left\langle k'\right|$$



$$J = \tfrac{ie}{\hbar}\left\langle c_i^+ c_{i+1} - h.c.\right\rangle$$

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





An open Quantum System Approach

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

Example 2 – Linear chain with two temperatures

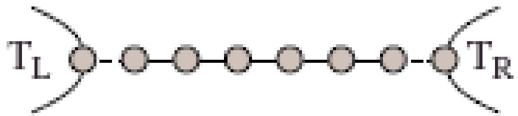
$$\dot{\hat{\rho}} = -i[\mathcal{H}, \hat{\rho}] + \mathcal{L}_{\mathrm{L}}\hat{\rho} + \mathcal{L}_{\mathrm{R}}\hat{\rho}$$

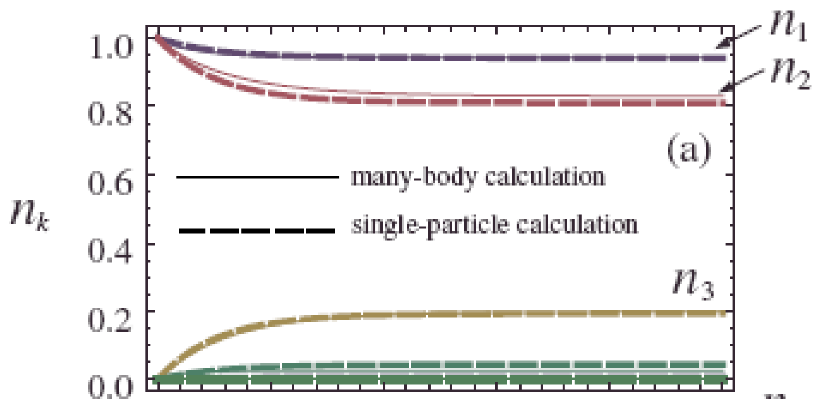
$$\mathcal{H} = -\sum_{i,j} t_{i,j} |i\rangle\langle j|$$

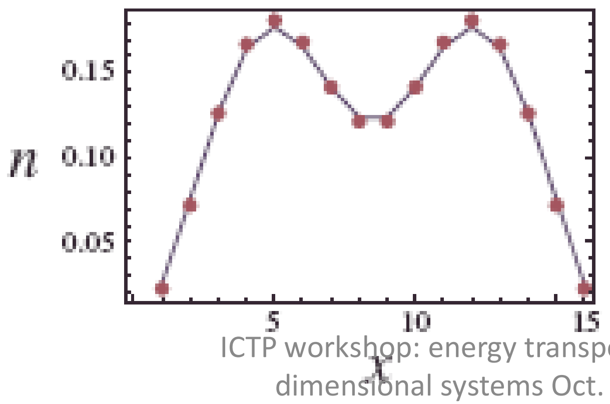
$$V_{kk'}^{(\mathrm{L,R})} = \sqrt{\gamma_{kk'}^{(\mathrm{L,R})} \; f_D^{(\mathrm{L,R})}(\varepsilon_k)} \, |k\rangle\langle k'|$$

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

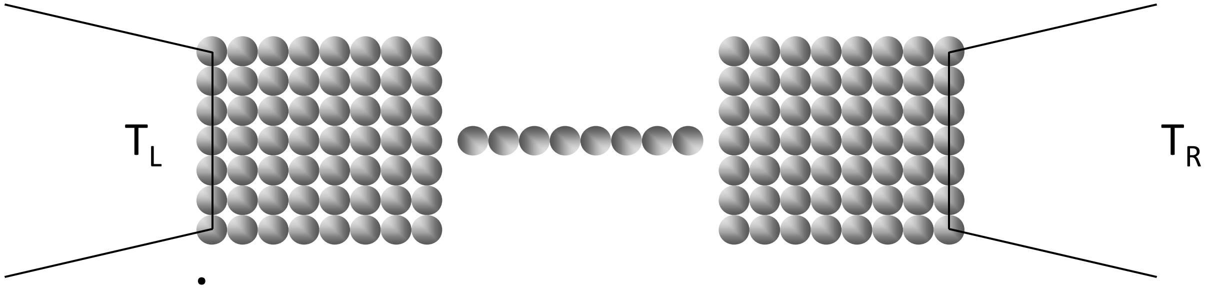
$$f_D^{(L,R)}(\varepsilon_k) = \frac{1}{\exp\left(\frac{\varepsilon_k - \mu_{L,R}}{T_{L,R}}\right) + 1}$$







Thermo-electric effects in a Nano Junction



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

Geometry Interactions → $\mathcal{H}$

Temperature From Left → $\mathcal{L}_{\mathrm{L}}$

Temperature From Right → $\mathcal{L}_{\mathrm{R}}$

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

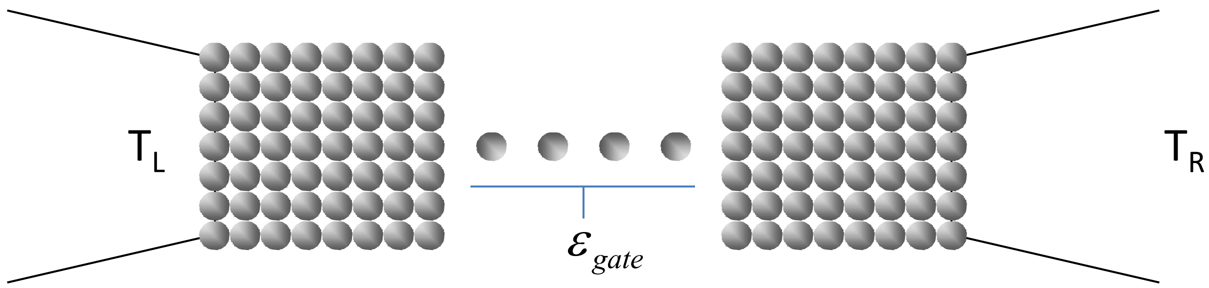
$L_x \times L_y = 28 \times 27$

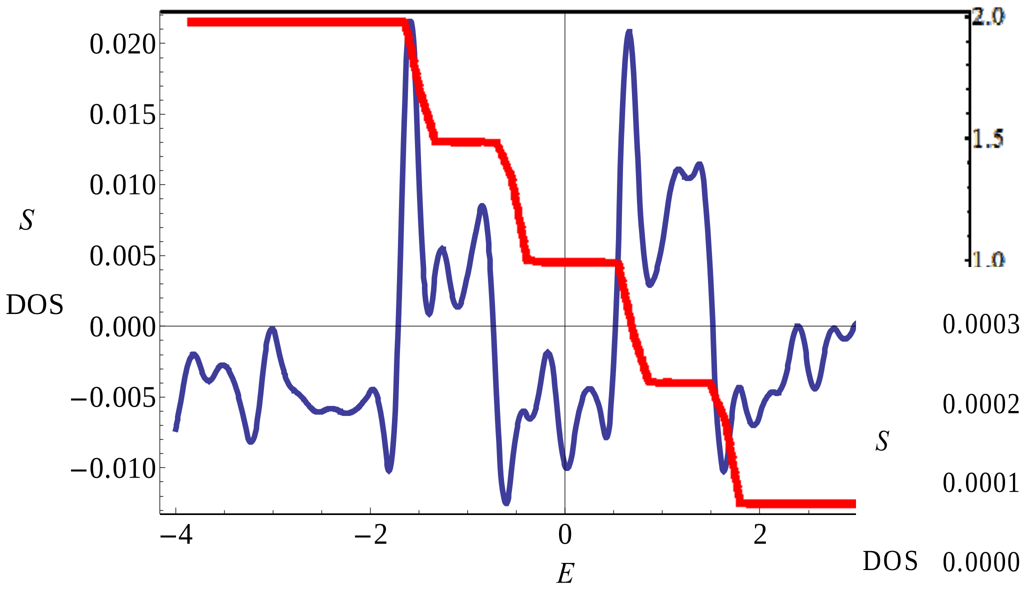
$L_d = 4$

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

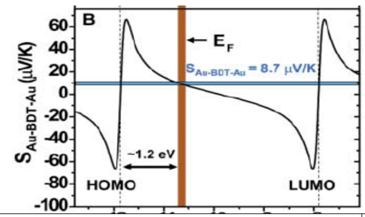
$g_L = g_R = 0.1$

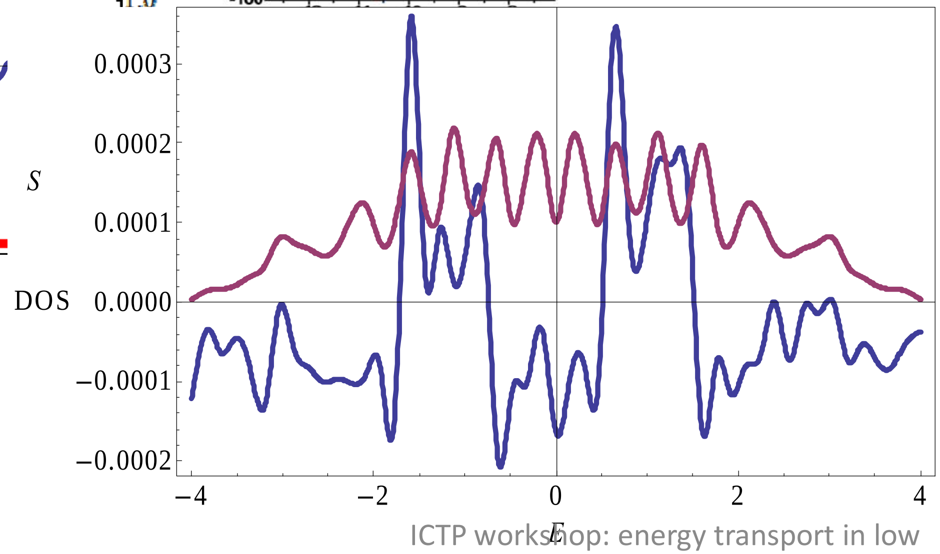
$T_L = RT$





Landauer resonant level:





Thermo-electric effects in a Nano Junction

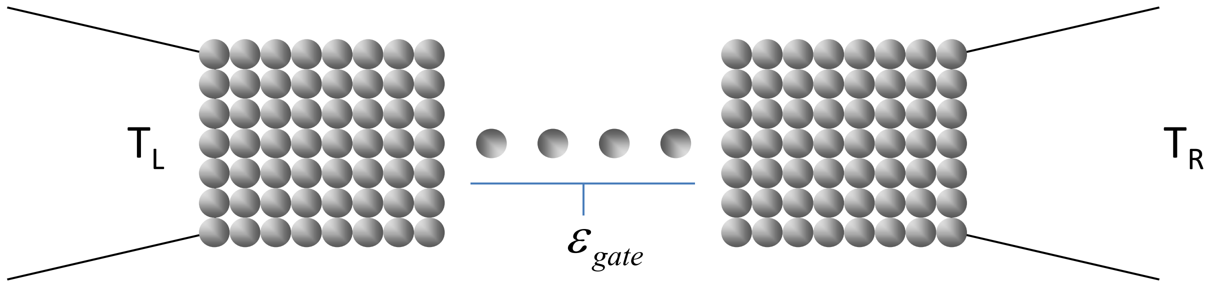
$L_x \times L_y = 20 \times 19$

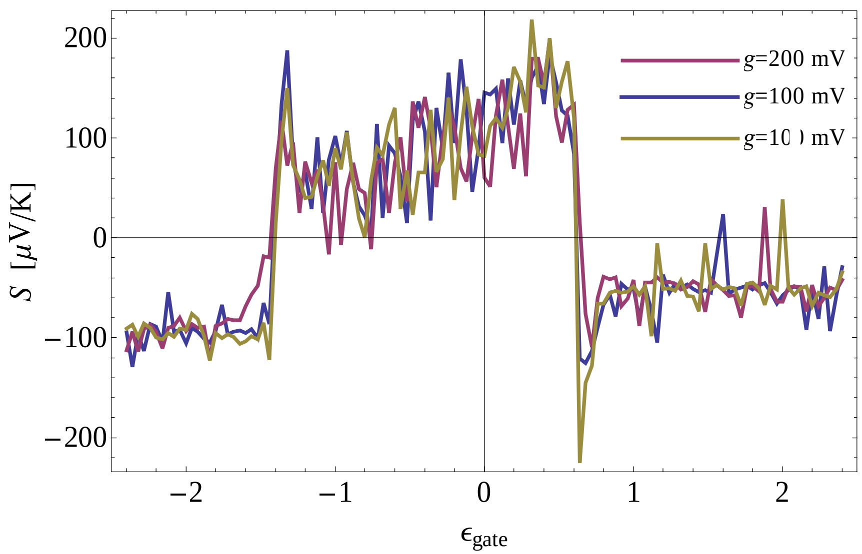
$L_d = 2$

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

$g_L = g_R = 0.1$

$T_L = RT$



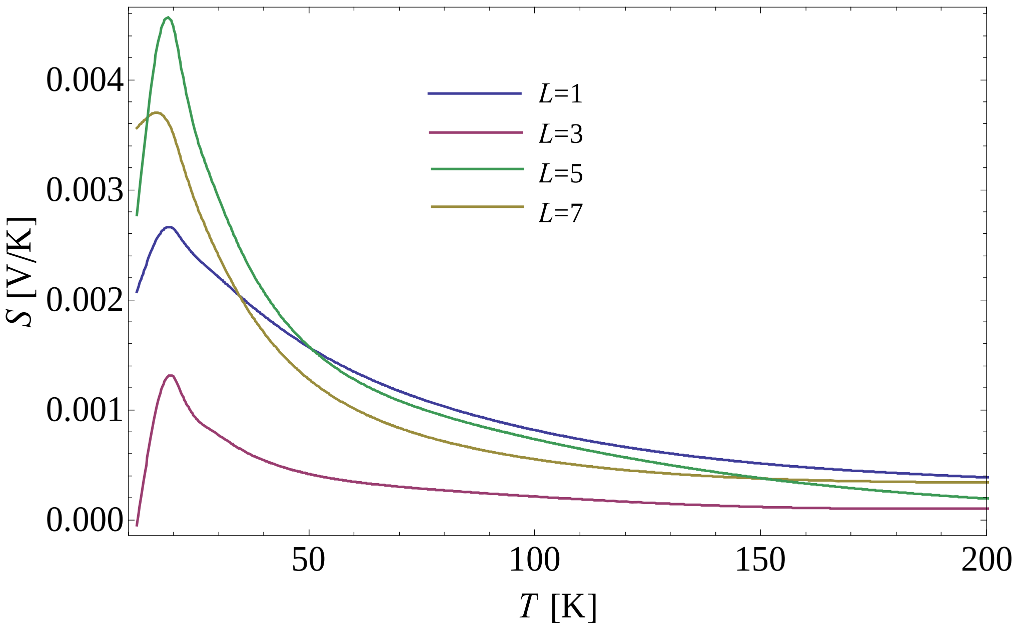


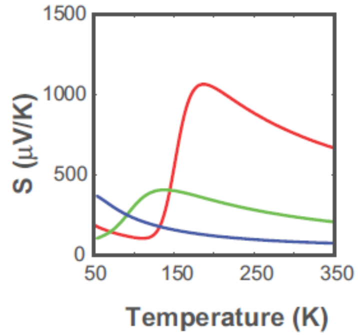
of the HOMO to the chemical potential. We also show that when the coupling of the molecule with one of the electrodes is reduced, the electrical conductance of junctions decreases dramatically, whereas the thermopower remains relatively invariant. Further, we show that

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

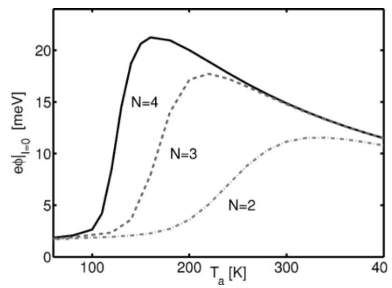
Thermo-electric effects in a Nano Junction

Non-homogeneous *T*-dependence
(coherent tunneling Vs. thermal activation)



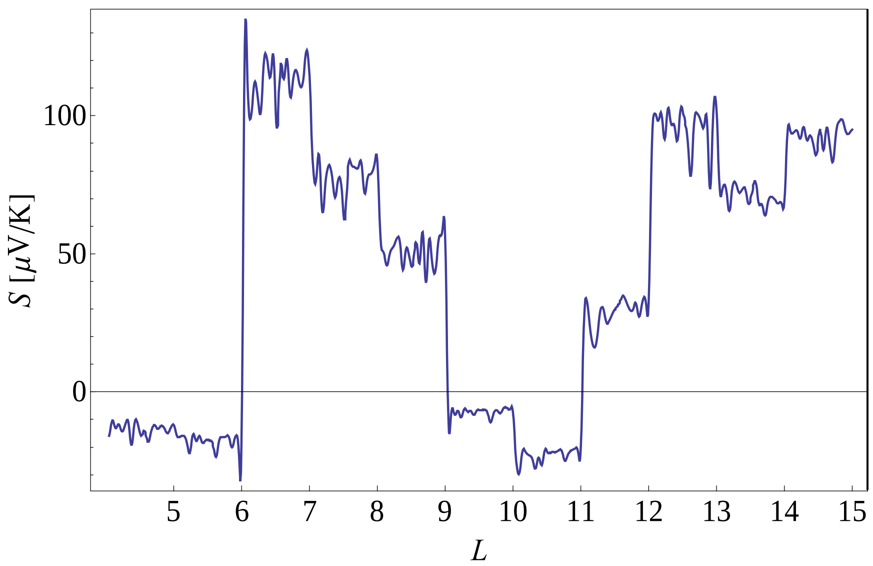


D. Nozaki *et al.*, PRB **81**, 235406 (2010)



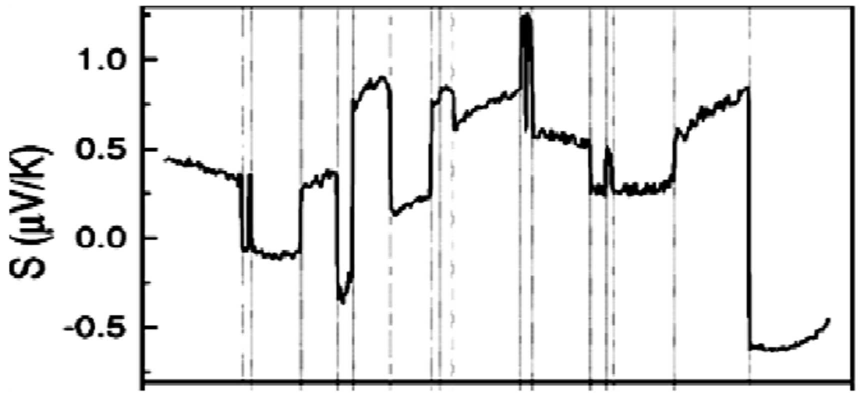
D. Segal, PRB **72**, 165426 (2005)

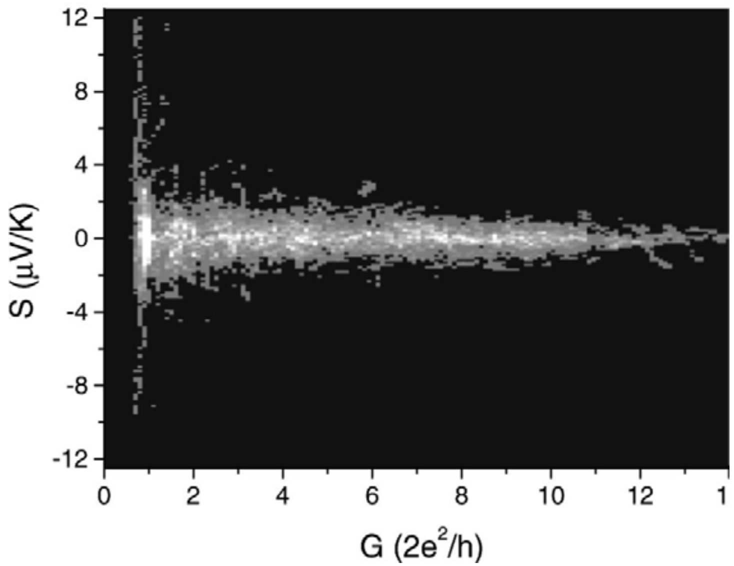
Thermo-electric effects in a Nano Junction



Increasing piezovoltage

Fluctuations in an atomic wire:





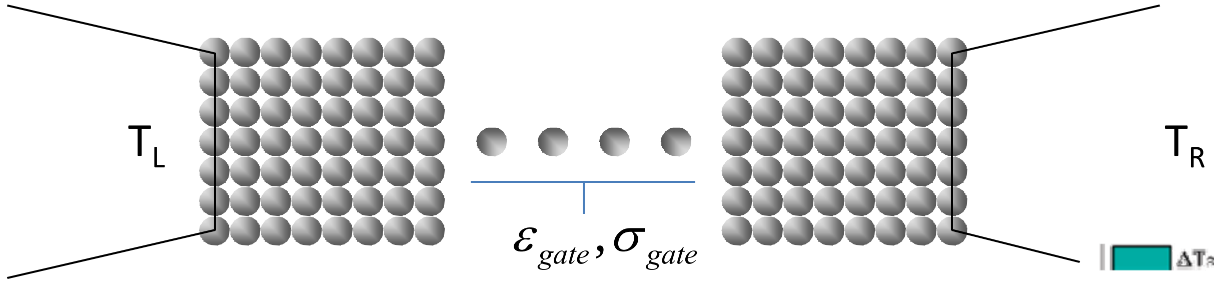
Thermo-electric effects in a Nano Junction

$L_x \times L_y = 20 \times 19$

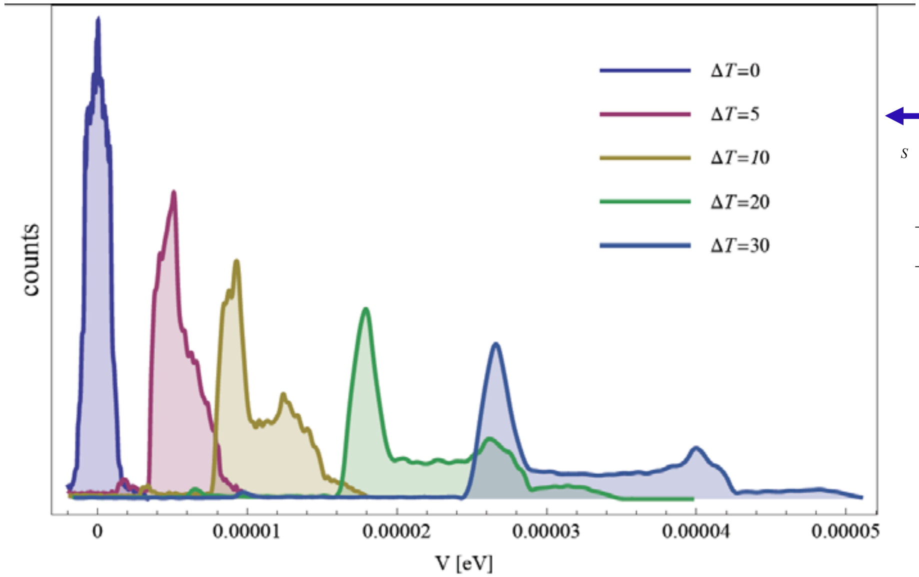
$n \sim 0.45$ (slightly below half - filling)

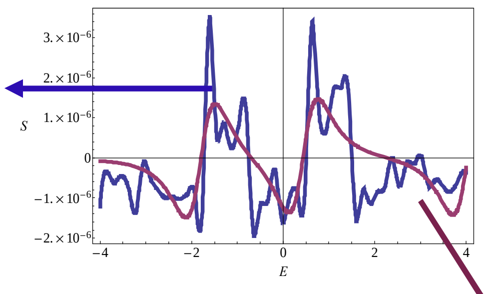
$g_L = g_R = 0.1$

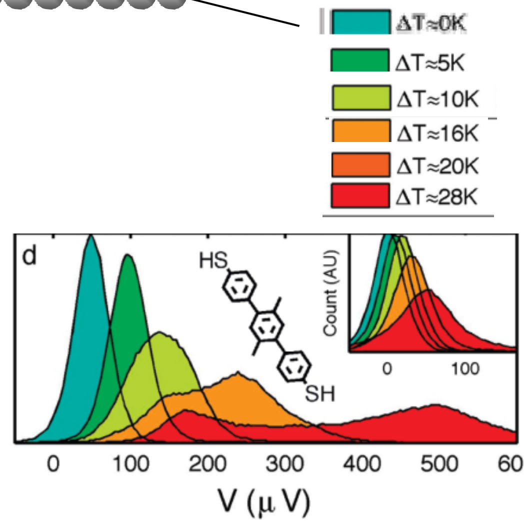
$T_L = RT$

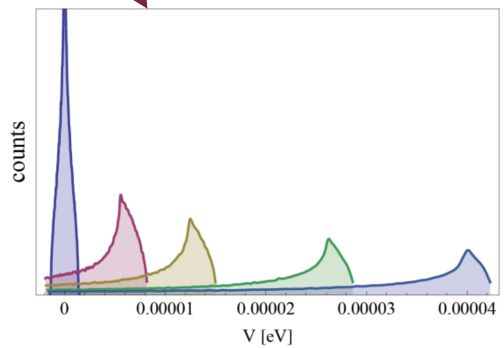


$\delta T = 2\text{K}, \ \sigma_{gate} = 0.2\text{eV}$









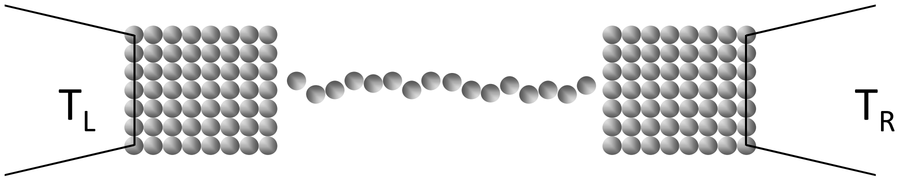
Conclusion:

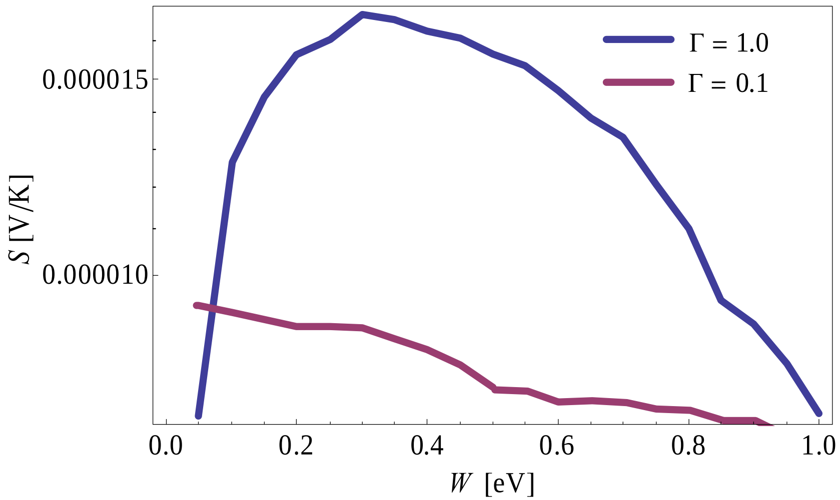
LDOS fluctuations at molecule-electrode interface are essential

Thermo-electric effects in a Nano Junction

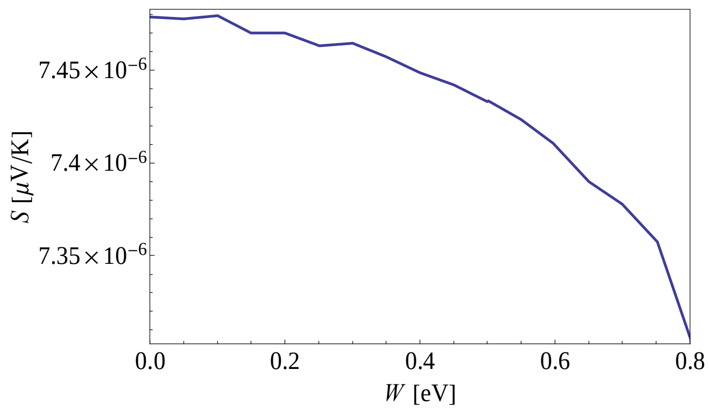
Effect of disorder - an open question

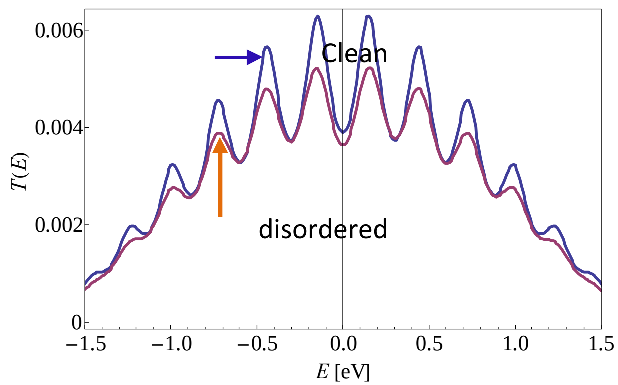
Effect of interaction?





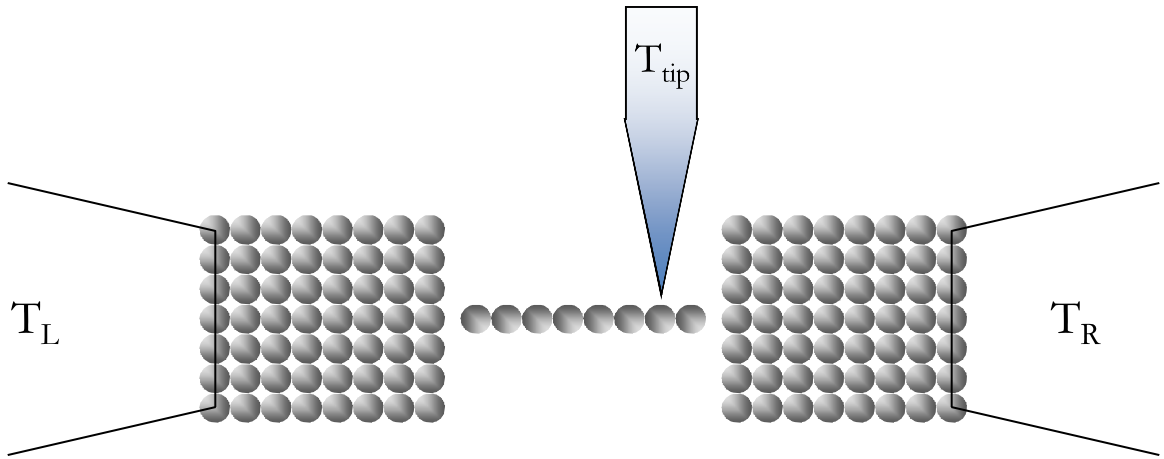
Landauer's formula:
Opposite prediction





Local temperature in a Nano Junction

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



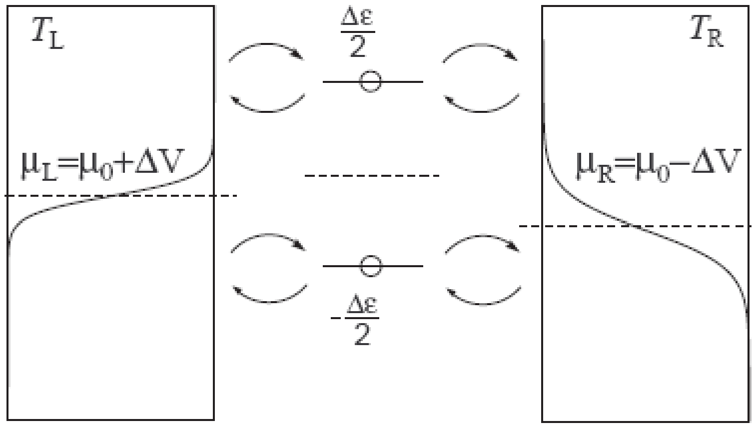
$$\dot{\hat{\rho}} = -i[\mathcal{H}, \hat{\rho}] + \mathcal{L}_L \hat{\rho} + \mathcal{L}_R \hat{\rho} + \mathcal{L}_{tip} \hat{\rho}$$

- 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

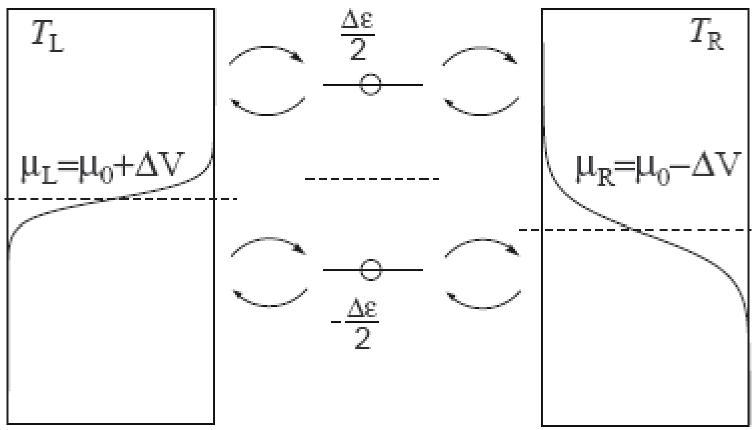
2^{nd} way to define T_{eff} :

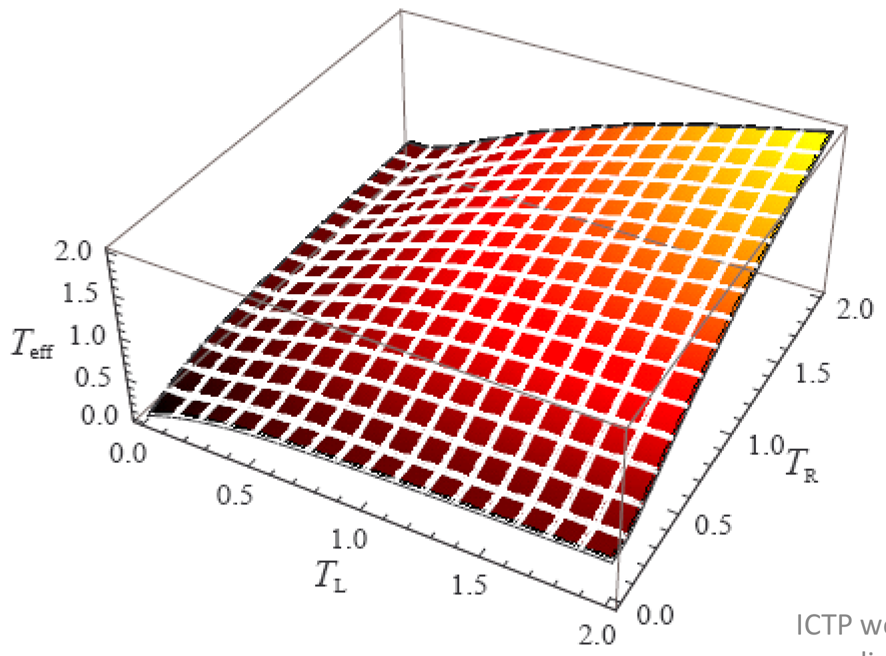
1. Include an additional tip with temperature T_{tip}

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

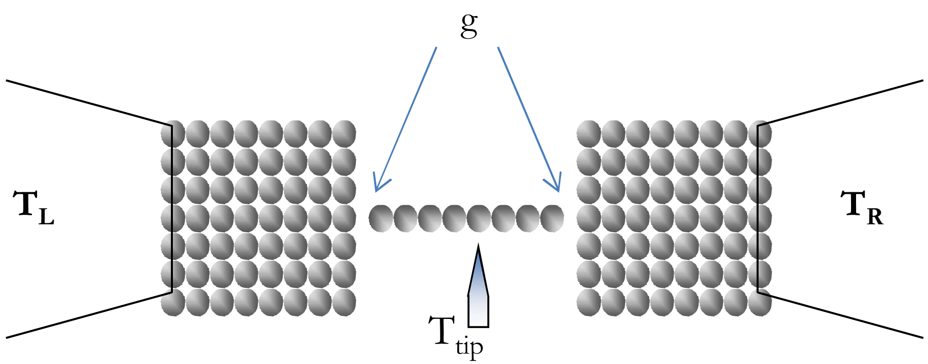
2. Make sure the tip doesn't change anything

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

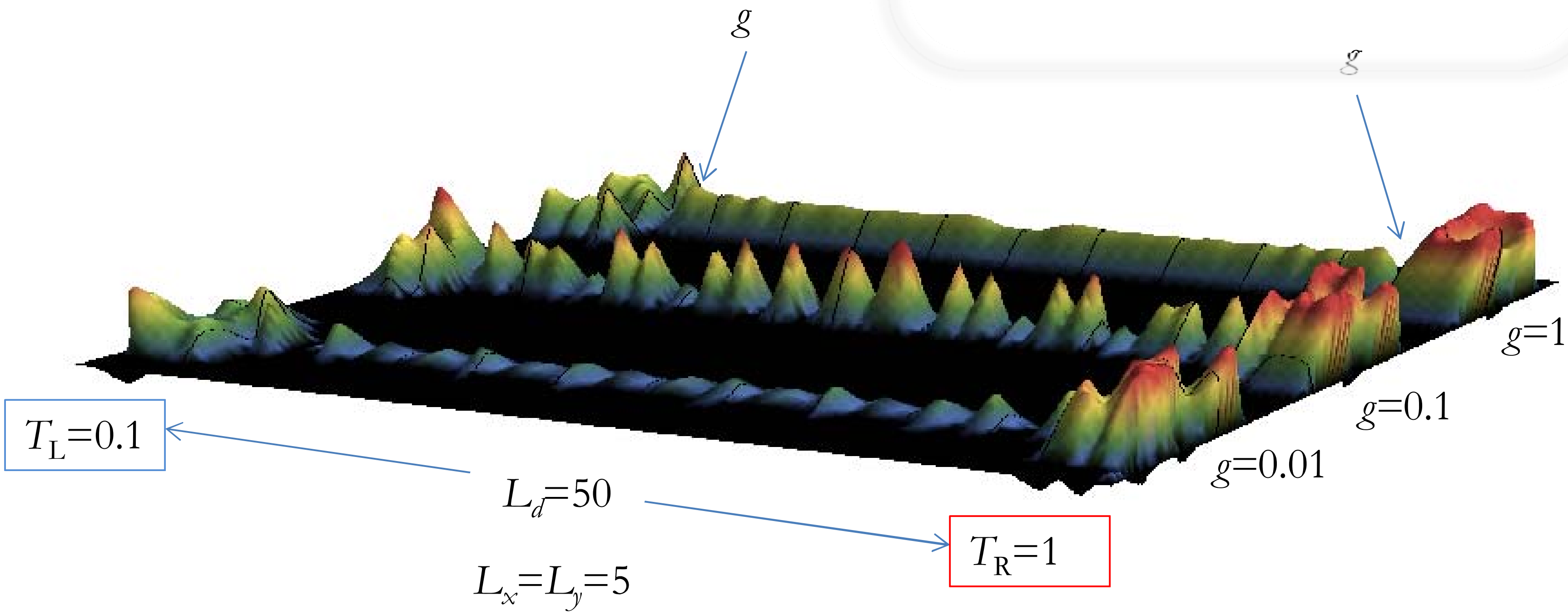




Local temperature in a Nano Junction



- Small *g* – lower temperature better coupled to wire
- Intermediate *g* – Temperature oscillations
- Large *g* – Uniform Temperature



J. B. J. Fourier
(1768 – 1830)

$$j = -k\nabla T$$

Energy current — Thermal conductivity — Temp. gradient

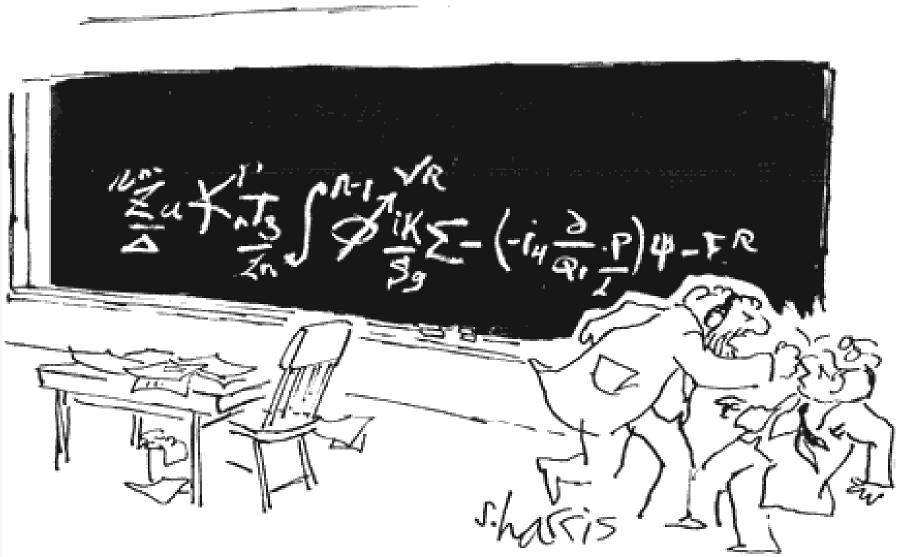
~200 years later…

FOURIER LAW: A CHALLENGE TO THEORISTS

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

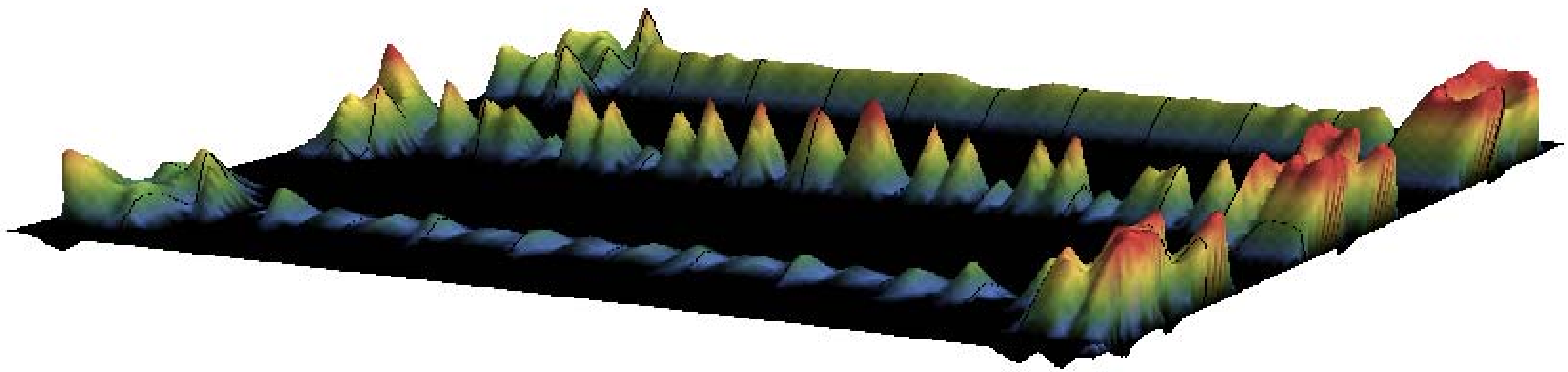
We present a selective overview of the current state of our knowledge (more precisely of our ignorance) regarding the derivation of Fourier's Law, $\mathbf{J}(\mathbf{r}) = -\kappa\nabla T(\mathbf{r})$; $\mathbf{J}$ the heat flux, T the temperature and κ, the heat conductivity. This law is empirically 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



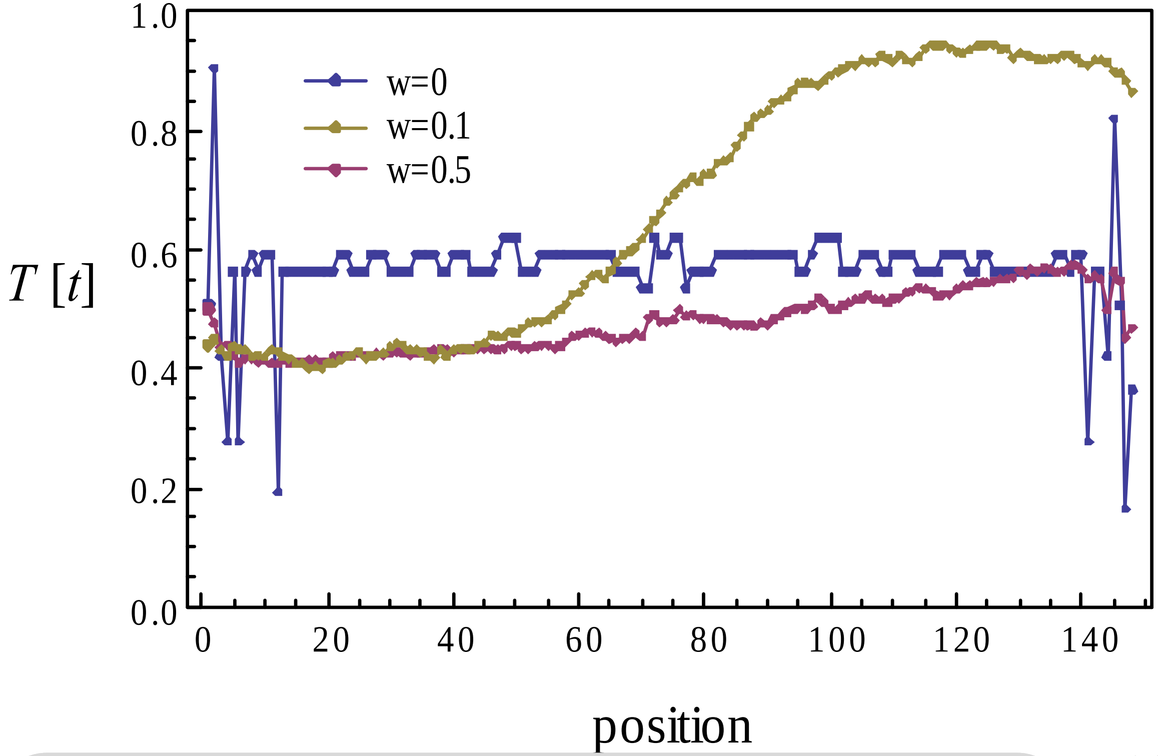
Conclusion I:

Breakdown of Fourier's law in ballistic quantum wires

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

Reconstructing Fourier's law from disorder

$$\mathcal{H} = -\sum_{i,j} t_{i,j}|i\rangle\langle j| + \sum_i \epsilon_i|i\rangle\langle i|, \qquad \epsilon_i \in N[0,W]$$

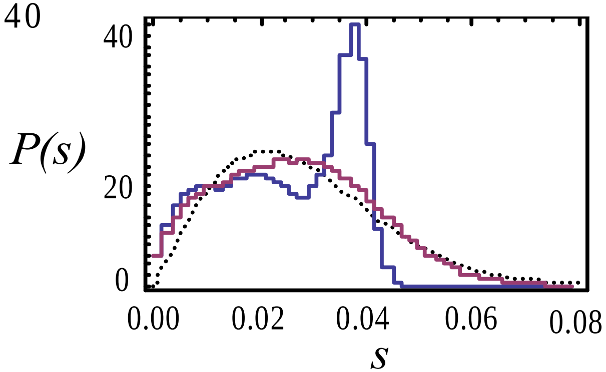


[Dubi & Di Ventra, PRB **79**, 115415 (2009)]

Conclusion II:

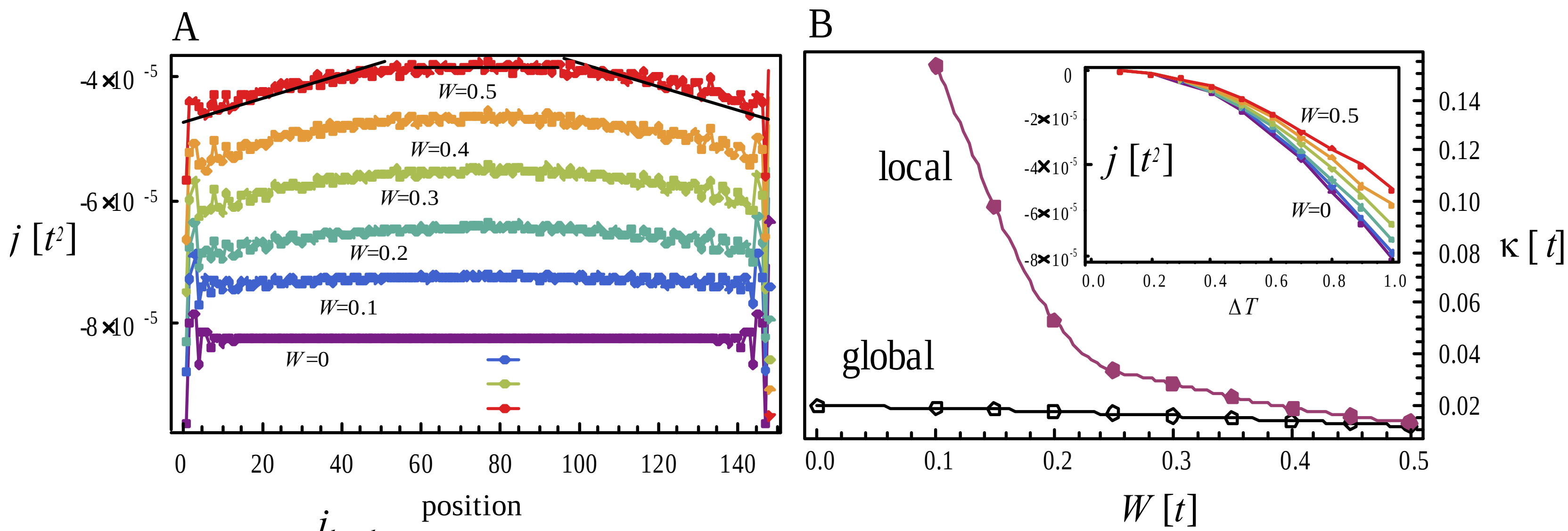
Fourier's law is reconstructed by disorder

(it seems to fit the onset of "Quantum Chaos")



Reconstructing Fourier's law from disorder

Local heat current and thermal conductivity



$$\kappa_{local} = \frac{j_{local}}{\nabla T_{local}}$$

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

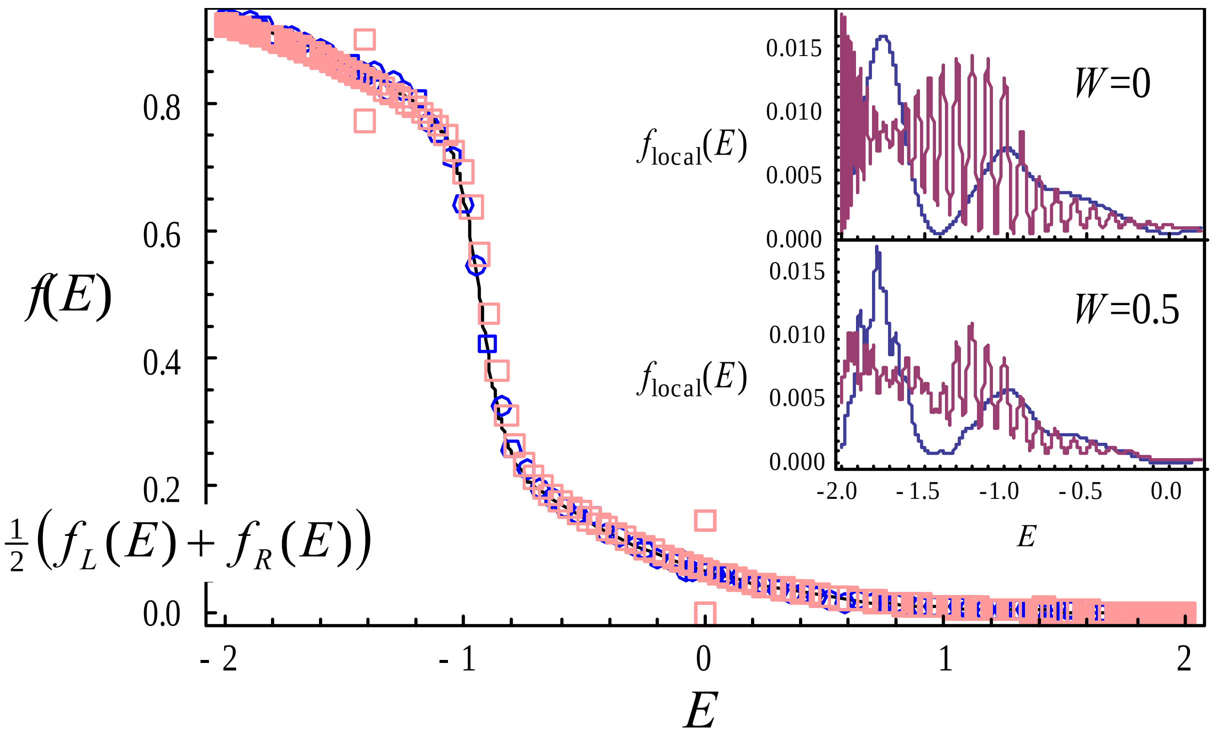
Conclusion III:

The onset of Fourier's law can be determined

by comparing the local and global thermal conductivities.

Role of disorder

Energy distribution function :



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

(Master equation +diagonal disorder)

Conclusion III:

The disorder affects the local properties, but does not affect the energy distribution function, which is determined from the “boundary conditions”.

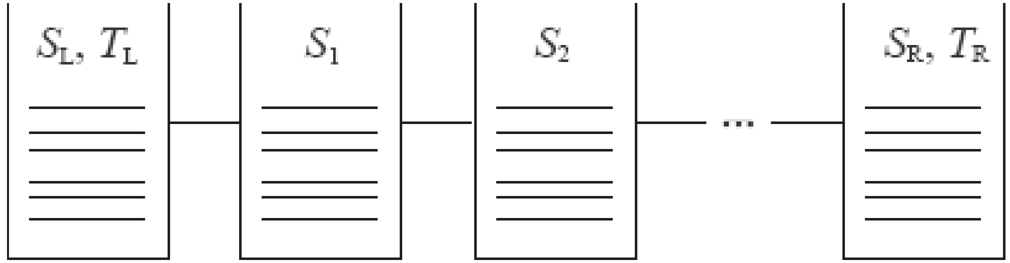
One cannot look for Fourier’s law by measuring local distribution functions.

Insight from a simple model

[Dubi and Di Ventra, PRE **79**, 042101 (2009)]

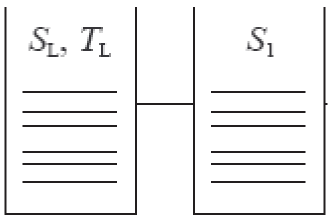
Assumptions :

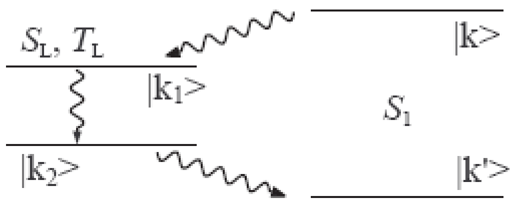
1. T_{L} and T_{R} fixed
2. Local equilibrium
3. Weak coupling



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

Step 1: only S_{L} and S_1



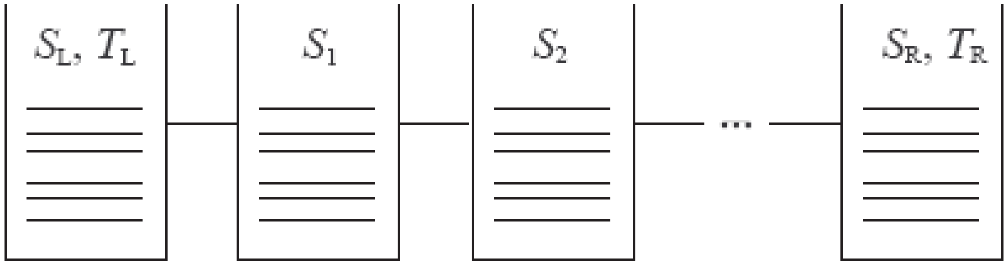


$$W^{(1)}_{k\to k'} = \sum_{k_1,k_2} \Gamma^{1\to \mathrm{L}}_{k\to k_1} W^{(\mathrm{L})}_{k_1\to k_2} \Gamma^{\mathrm{L}\to 1}_{k_2\to k'}$$

$$\downarrow$$

$$W^{(1)}_{k\to k'} = \gamma W^{(\mathrm{L})}_{k\to k'}$$

Insight from a simple model



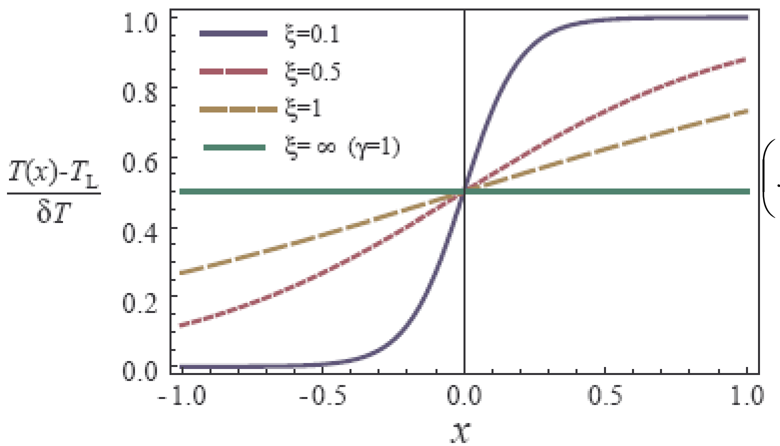
Step 2: considering S_L and S_1, S_2… S_n → $$W^{(n)}_{k\to k'} = \gamma^n W^{(L)}_{k\to k'}$$

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

Definition of T_n : $\frac{W^{(n)}_{k\to k'}}{W^{(n)}_{k'\to k'}} \exp\left(\frac{\Delta E_{kk'}}{k_B T_n}\right)$, $\forall$k, k'

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

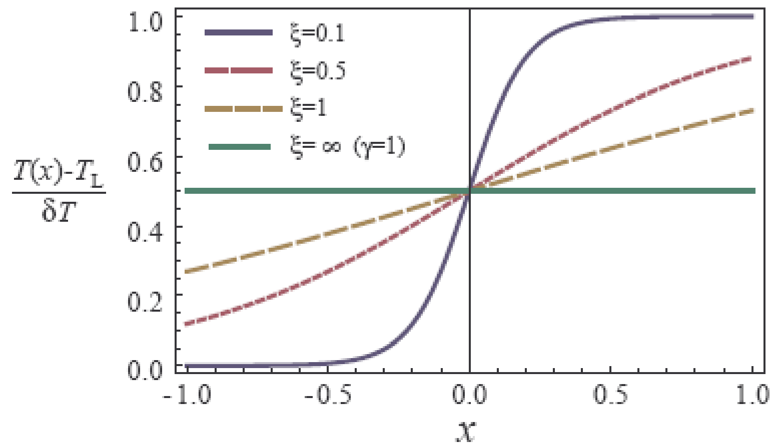
$$= T_L + \frac{1}{1+\exp(x/\xi)}\delta T \quad , \xi = (N \log\gamma)^{-1}$$

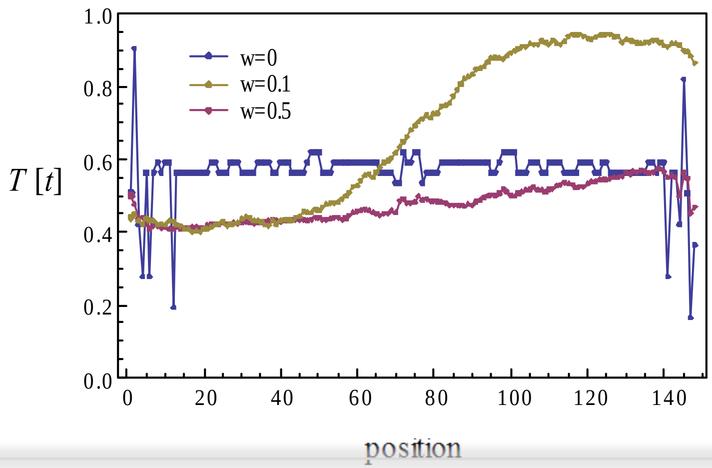


$\left(x = \frac{2n}{N} - 1\right)$

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

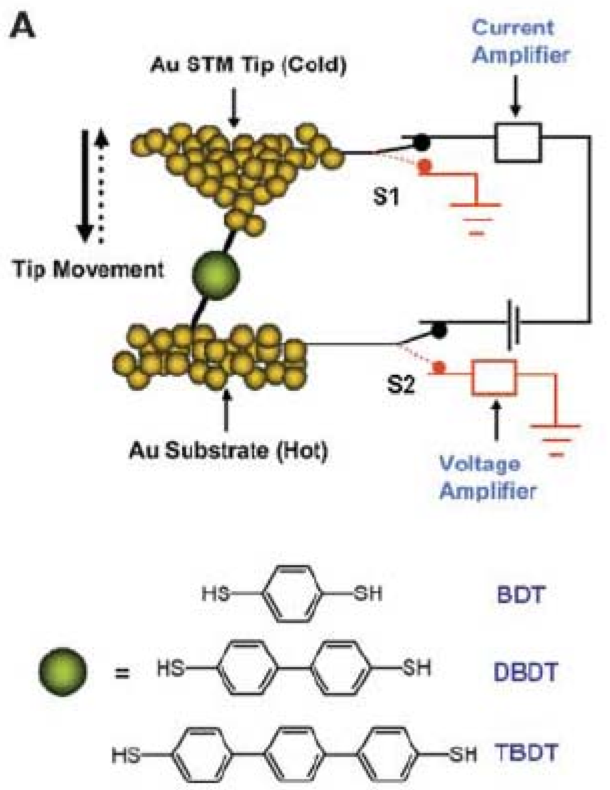
(if dephasing is included, L_φ replaces ξ and we get the classical Fourier's law :

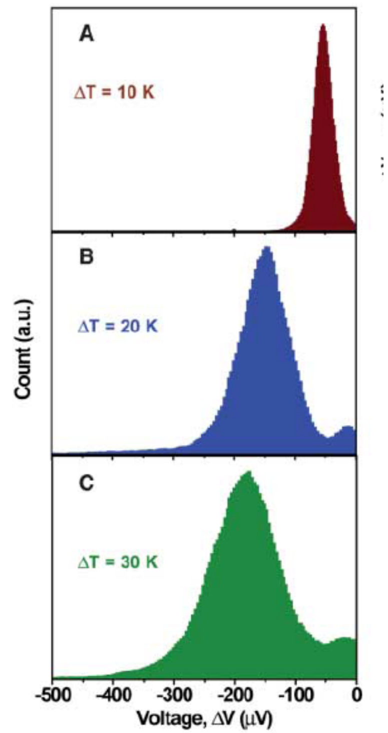
$$T_n = T_L + \frac{n}{N_{eff}}\delta T, \quad N_{eff} = \frac{N}{L_\varphi} \;)$$

SUMMARY: **ADVANCED WORKSHOP ON ENERGY TRANSPORT IN LOW-DIMENSIONAL SYSTEMS: Achievements and Mysteries**

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

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





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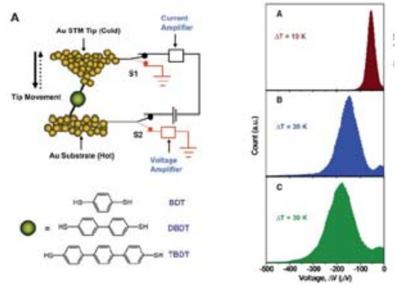
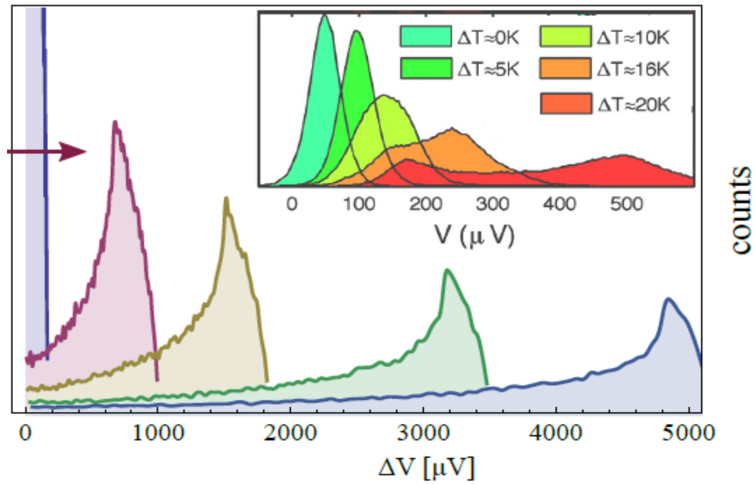


- Experiments of thermo-electricity in molecular junctions are certainly *achievements* and contain several *mysteries*
- Conventional methods (rate equations, NEGF) seem to miss something…



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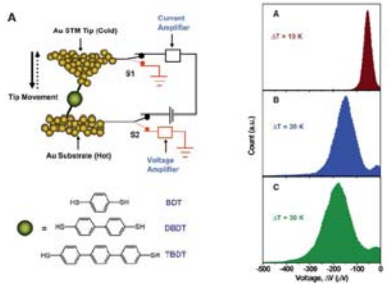

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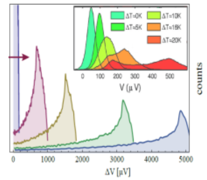
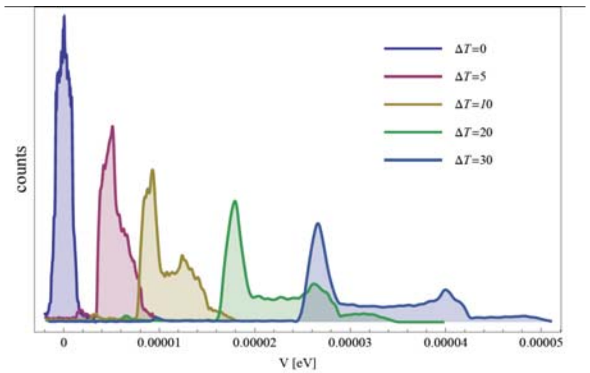
- ‘Open Quantum systems’ is a good approach to study TE in molecular junctions





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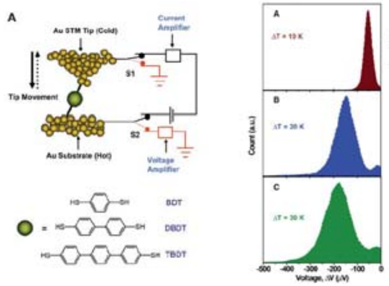

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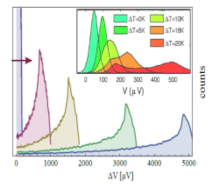

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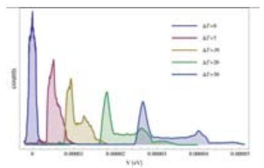
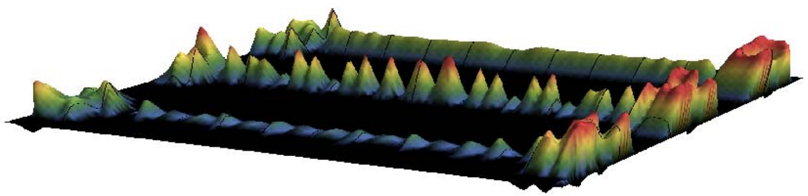


- And it can be used for other things too (e.g. local T)



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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*?