Thermoelectric enhancement in molecular junctions

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Outline

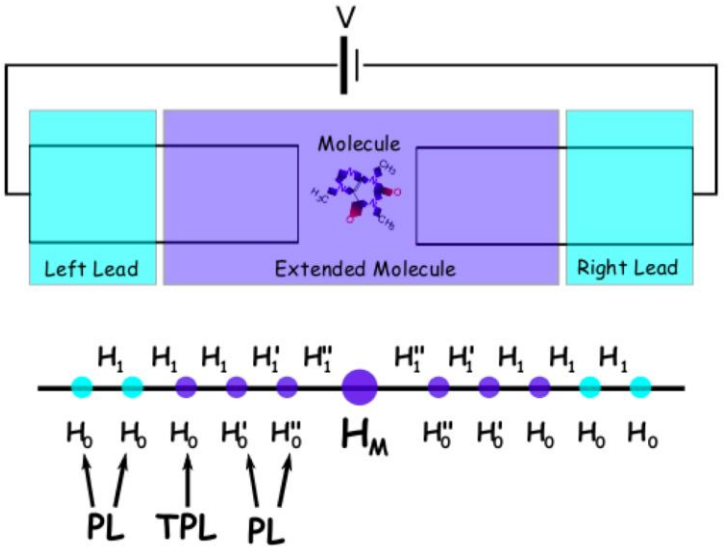
1) The GOLLUM code

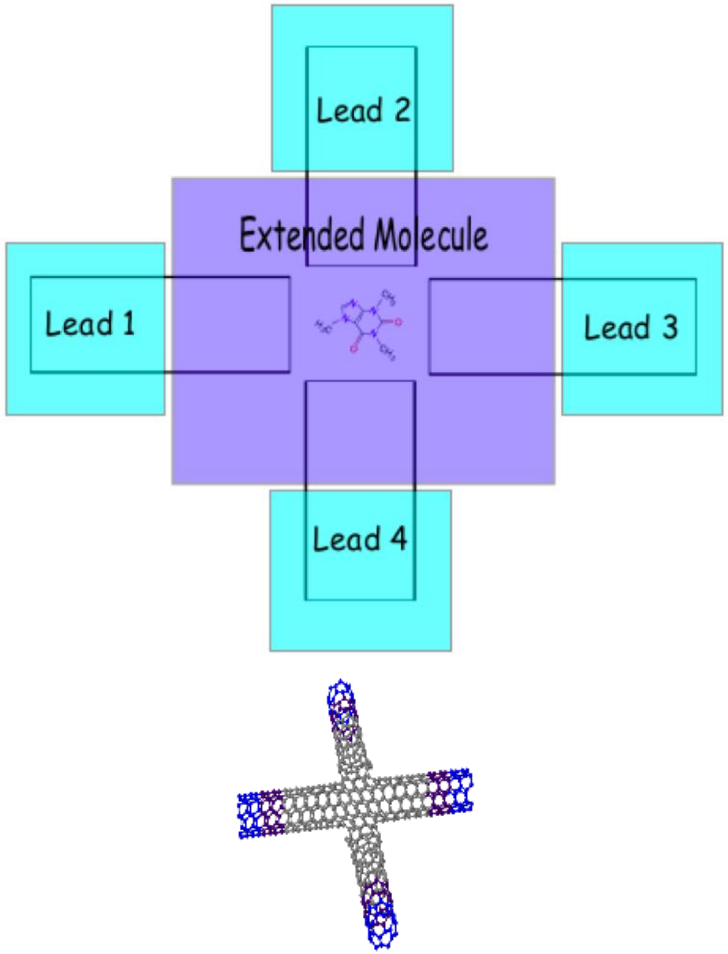
2) Thermoelectric properties of molecular junctions

3) Symmetry-induced thermoelectric effects

1) Introduction. The GOLLUM code

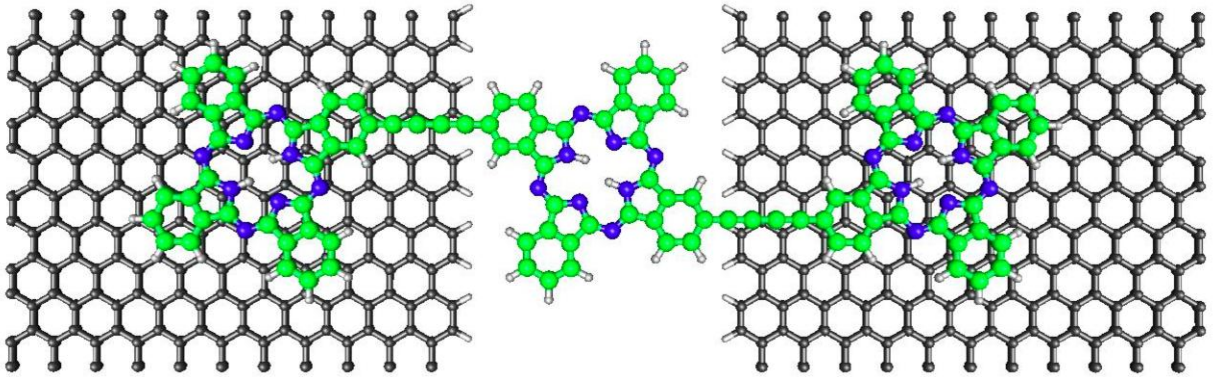
- Equilibrium and ab-initio-code-independent



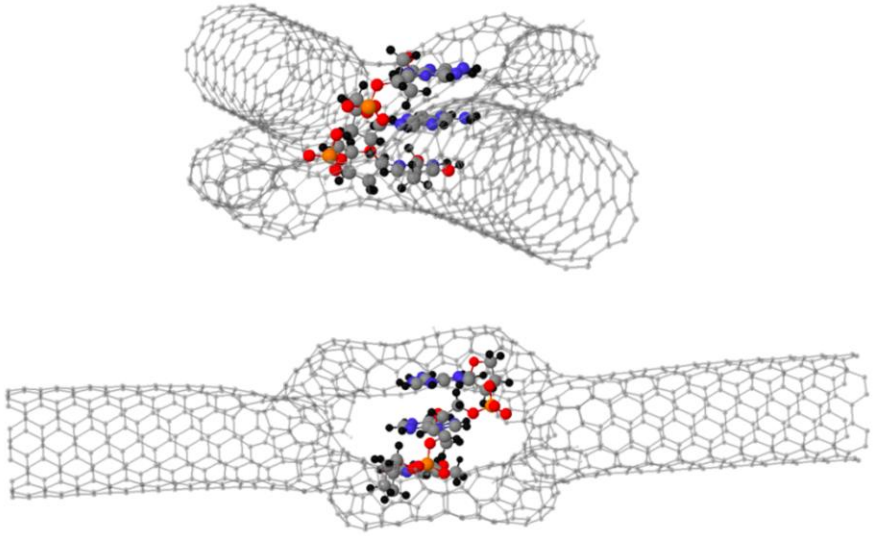


From 2 to 4 electrodes

- Large scale simulations

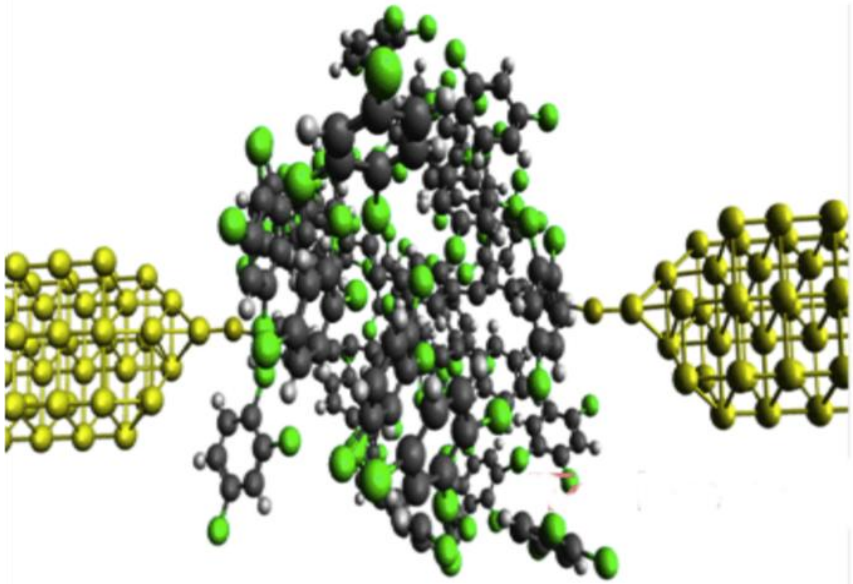


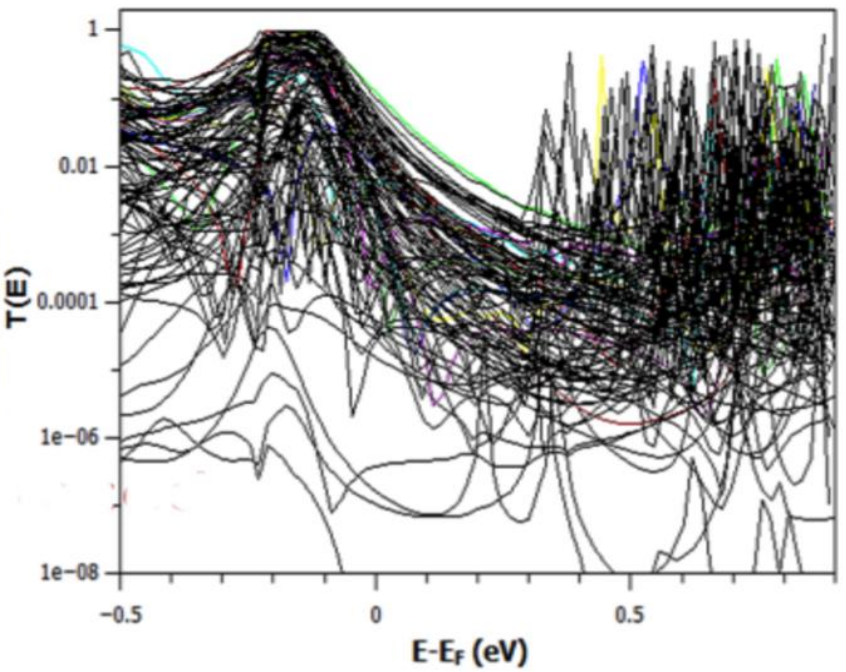
Graphene break junctions

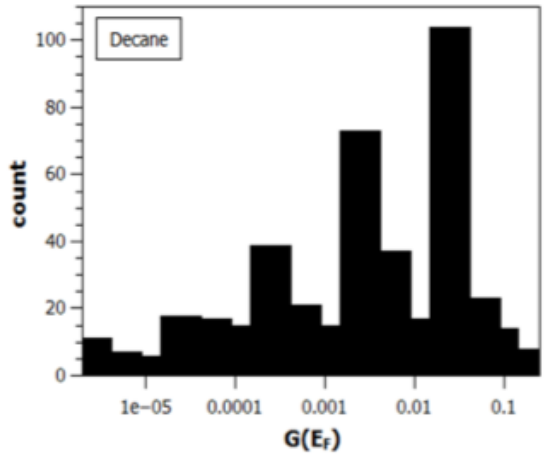


DNA sequencing nanopores (L. A. Algharagholy ,H. Sadeghi)

- Multi-scale simulations

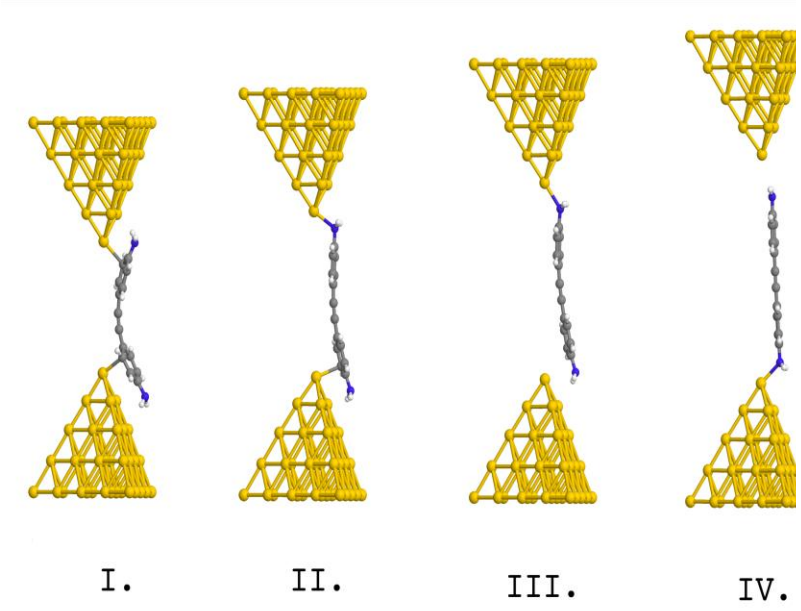


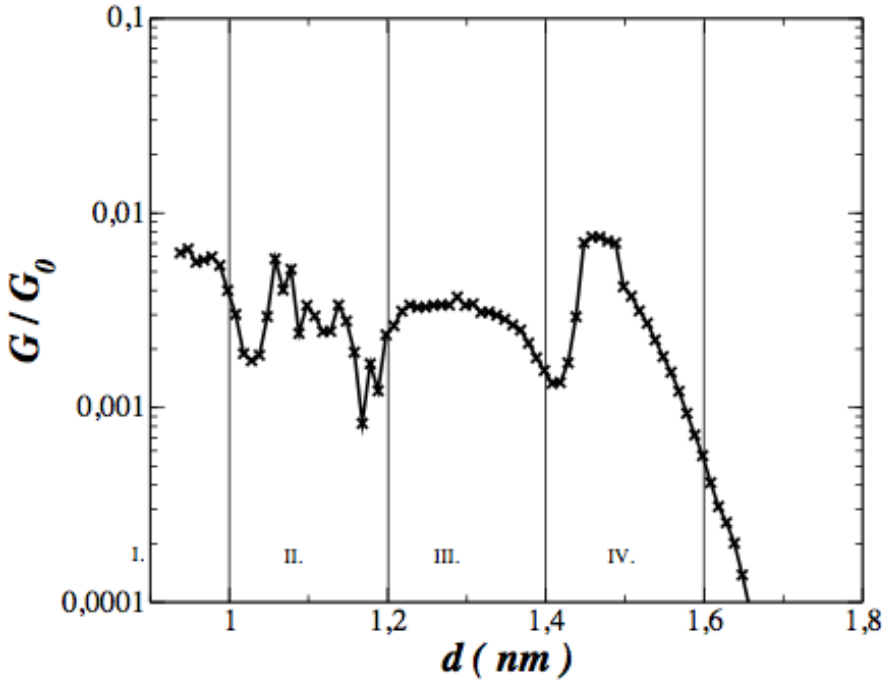




Transport properties of molecules in solvents (D. Manrique, I. Grace)

- Pulling curves

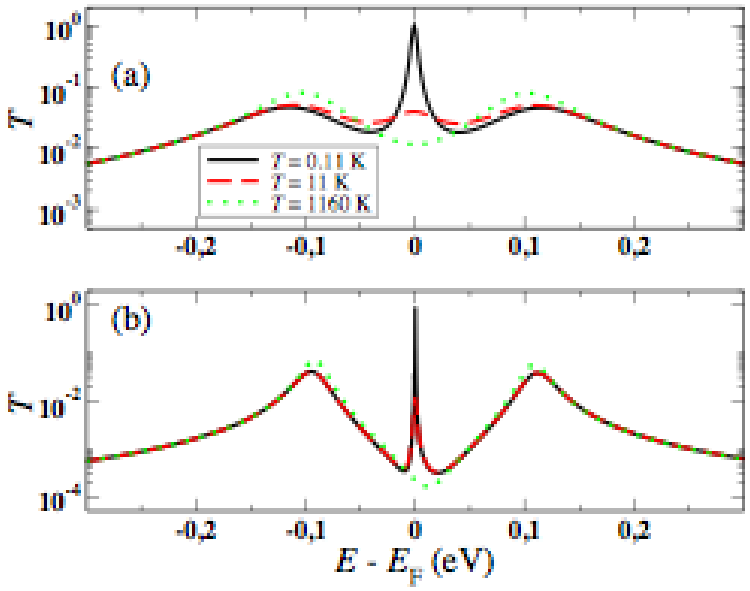


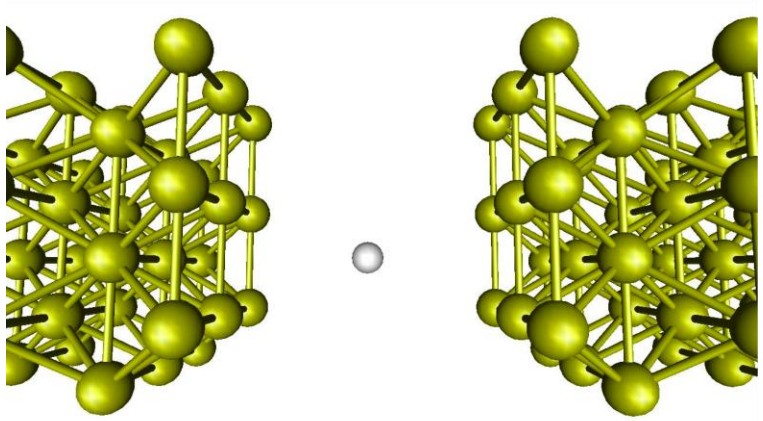


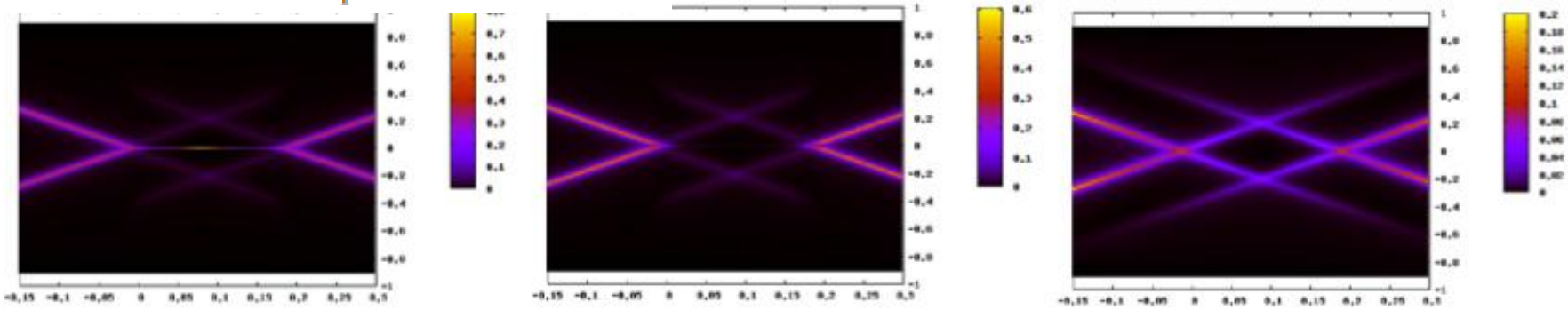
Conductance as a function of distance. MCBJ experiments (D. Manrique)

- Kondo and Coulomb blockade

Part of the system is strongly correlated

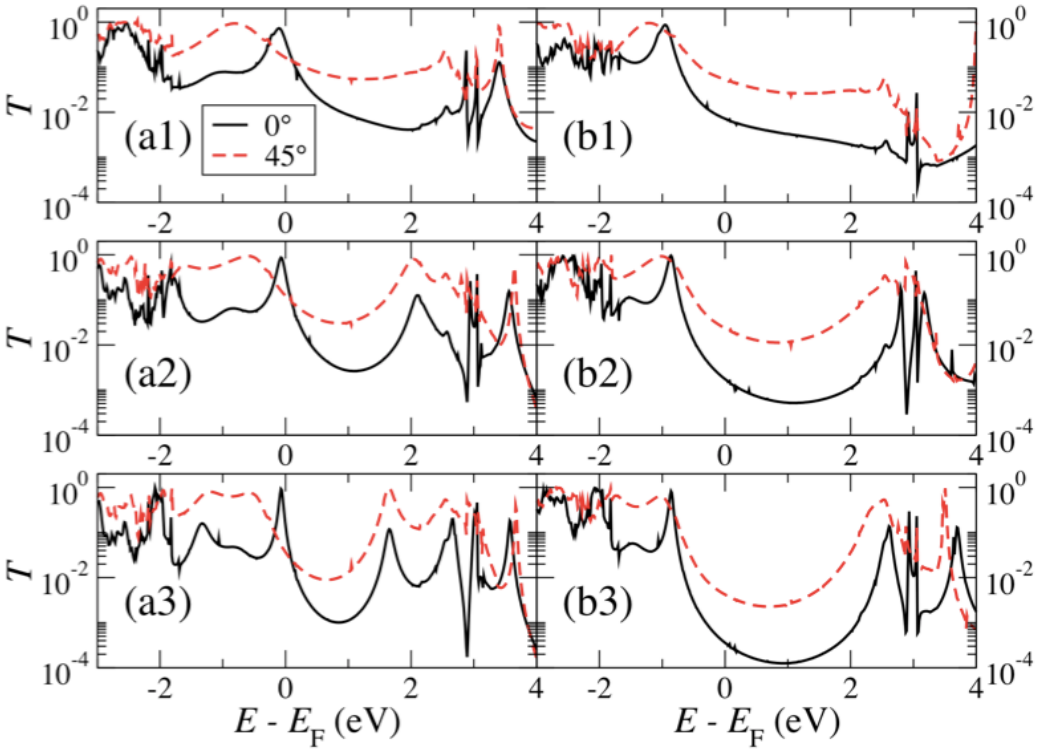


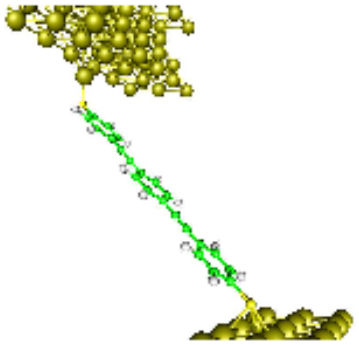


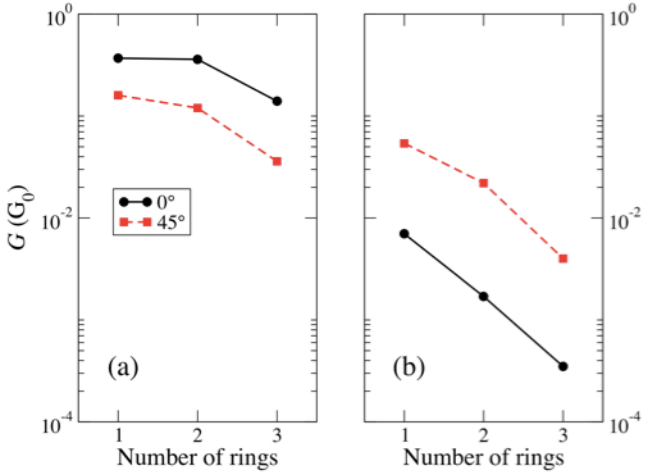


Also, LDA+U

- Spectral adjustment

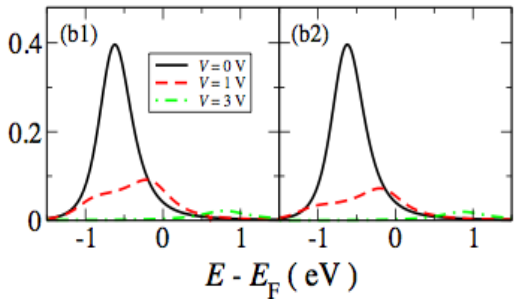




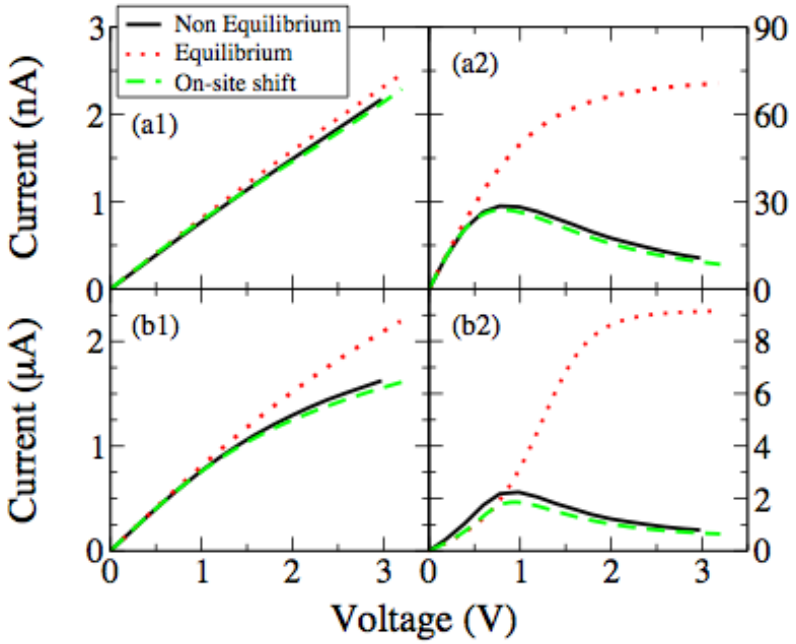


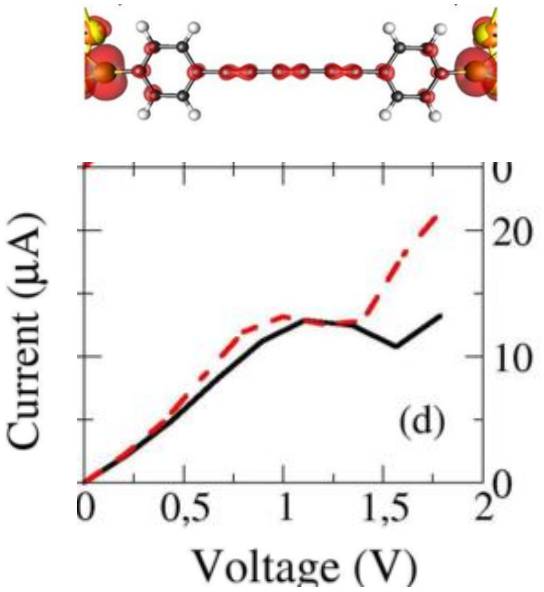
Quantitative and qualitative changes in the transport properties

- I-V characteristics



Non-equilibrium effects. NDR and non-trivial I-V characteristics

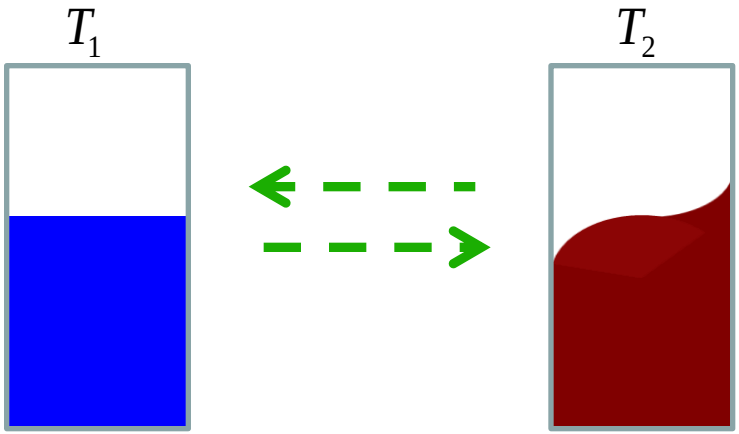




- Other things: phonon transport, superconductivity, etc.

2) Thermoelectric properties of molecular junctions

- Two electron reservoirs at different temperature



$T_1 < T_2$

The direction of electron flow depends on the transmission

$$\begin{pmatrix} \Delta V \\ \dot{Q} \end{pmatrix} = \begin{pmatrix} 1/G & S \\ \Pi & \kappa \end{pmatrix} \begin{pmatrix} I \\ \Delta T \end{pmatrix} \qquad G = \frac{2e^2}{h} L_0 \qquad S = \frac{-1}{eT} \frac{L_1}{L_0} \qquad \Pi = \frac{1}{e} \frac{L_1}{L_0} \qquad \kappa = \frac{2}{hT} \left(L_2 - \frac{L_1^2}{L_0} \right)$$

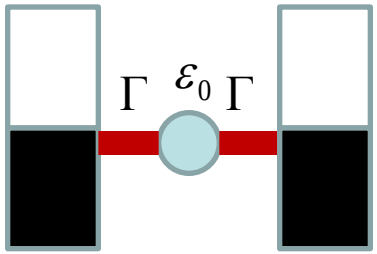
$$L_n = \int_{-\infty}^{\infty} (E - E_F)^n T(E) \frac{\partial f(E,V,T)}{\partial E} \mathrm{d}E$$

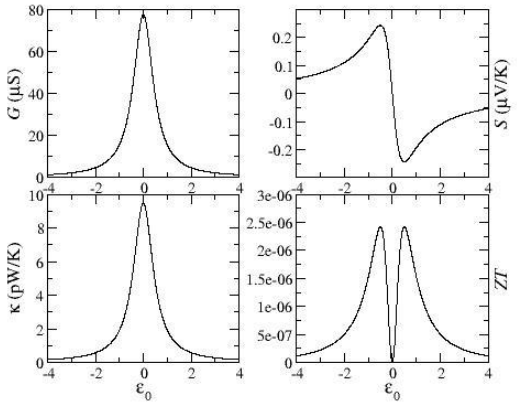
Figure of merit. Efficiency of heat to current converters

$$ZT = \frac{S^2 G T}{\kappa} = \frac{1}{\frac{L_0 L_2}{L_1^2} - 1}$$

- Interference-driven thermoelectricity

Breit-Wigner

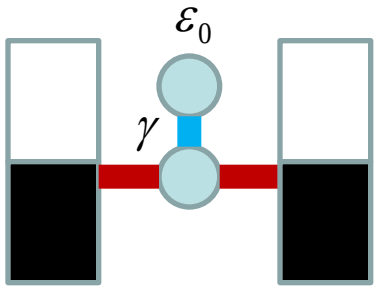


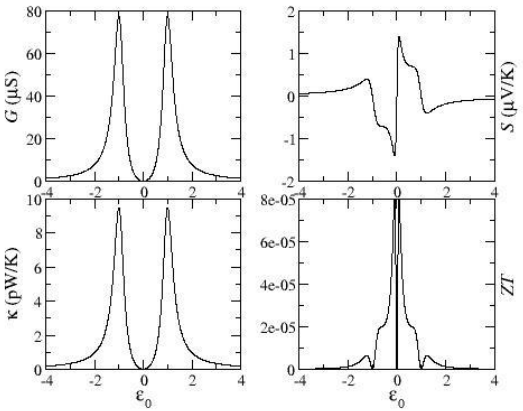


$$S = \frac{-1}{eT} S_0 \frac{2\varepsilon_0}{\varepsilon_0^2 + \Gamma^2}$$

$$ZT = \frac{4 S_0 \varepsilon_0^2}{(\varepsilon_0^2 + \Gamma^2)^2 - 4 S_0 \varepsilon_0^2}$$

Fano

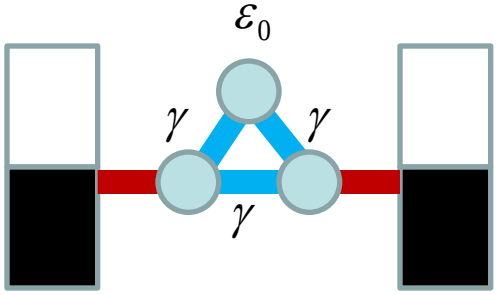


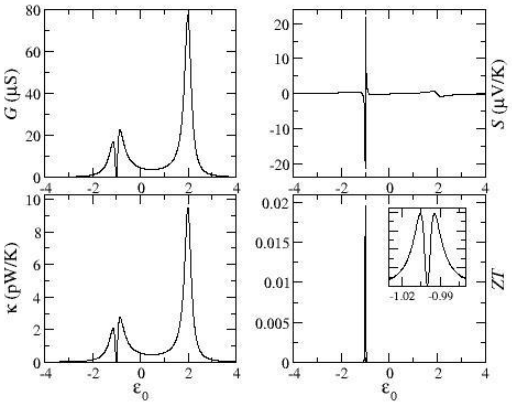


$$S = \frac{-1}{eT} S_0 \frac{\Delta(0)}{\varepsilon_0 \Gamma^2}$$

$$ZT = \frac{S_0 \Delta^2(0)}{\varepsilon_0^2 \Gamma^4 - S_0 \Delta^2(0)}$$

Multiple path



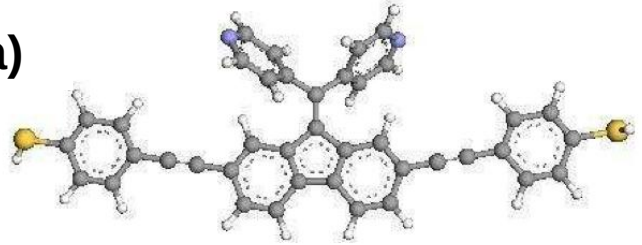


$$S = \frac{-1}{eT} S_0 \frac{\Lambda(0)}{t^2(0)\Gamma^2}$$

$$ZT = \frac{S_0 \Lambda^2(0)}{t^4(0)\Gamma^4 - S_0 \Lambda^2(0)}$$

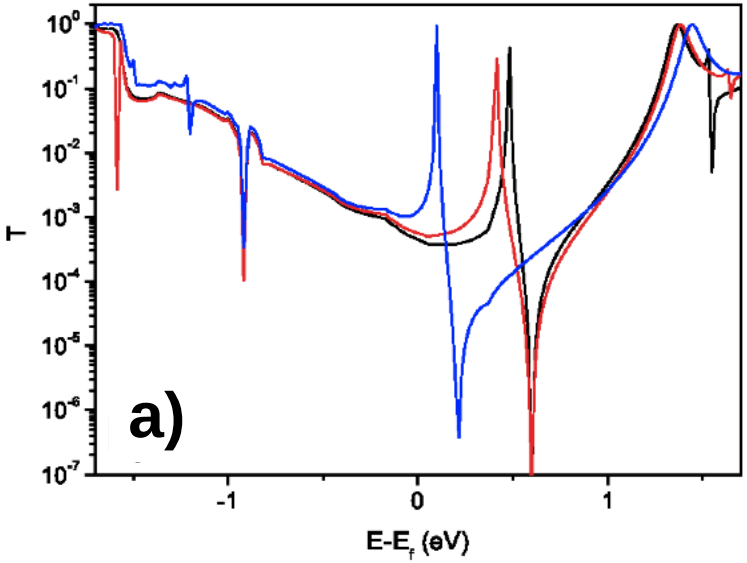
- OPE molecule with rotating rings or side groups

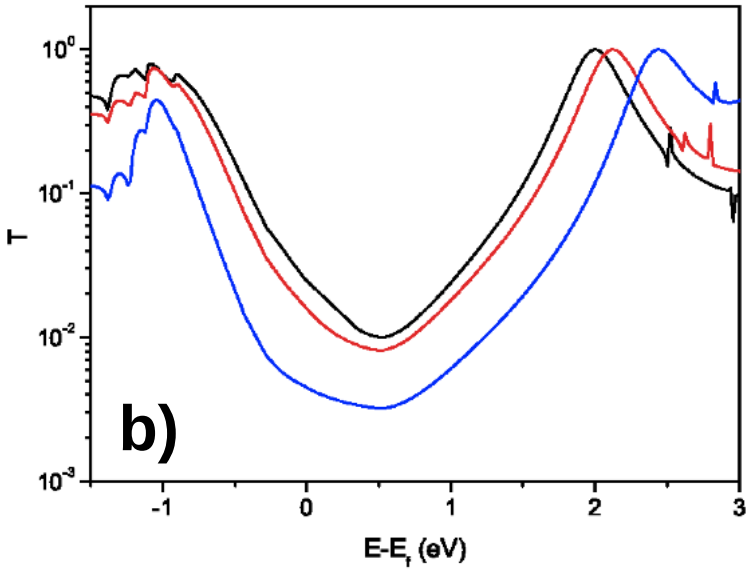
a)



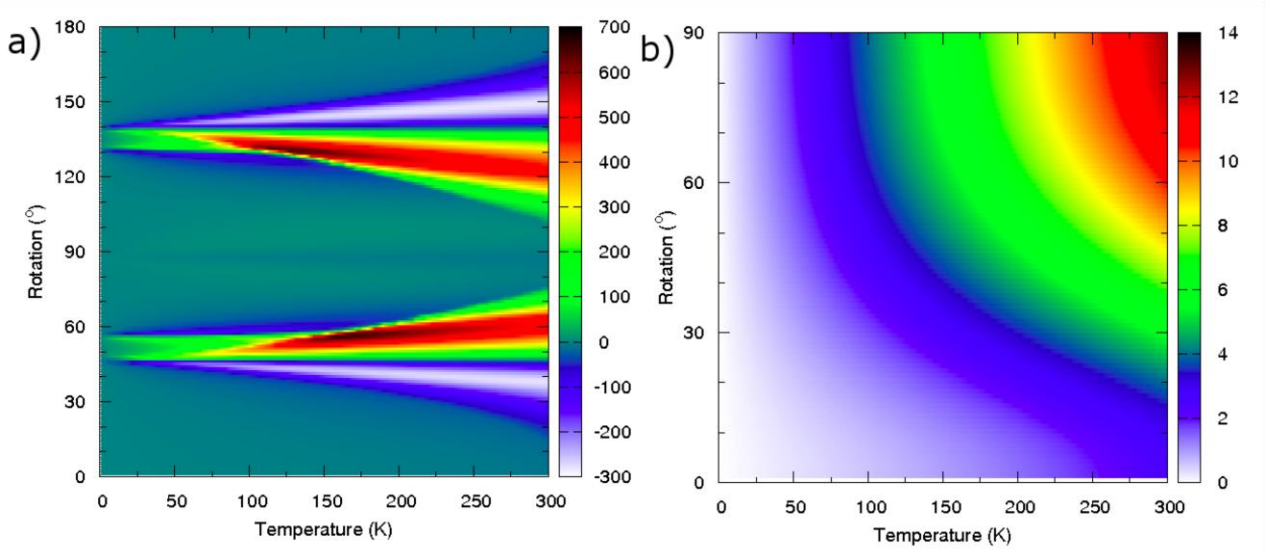
b)

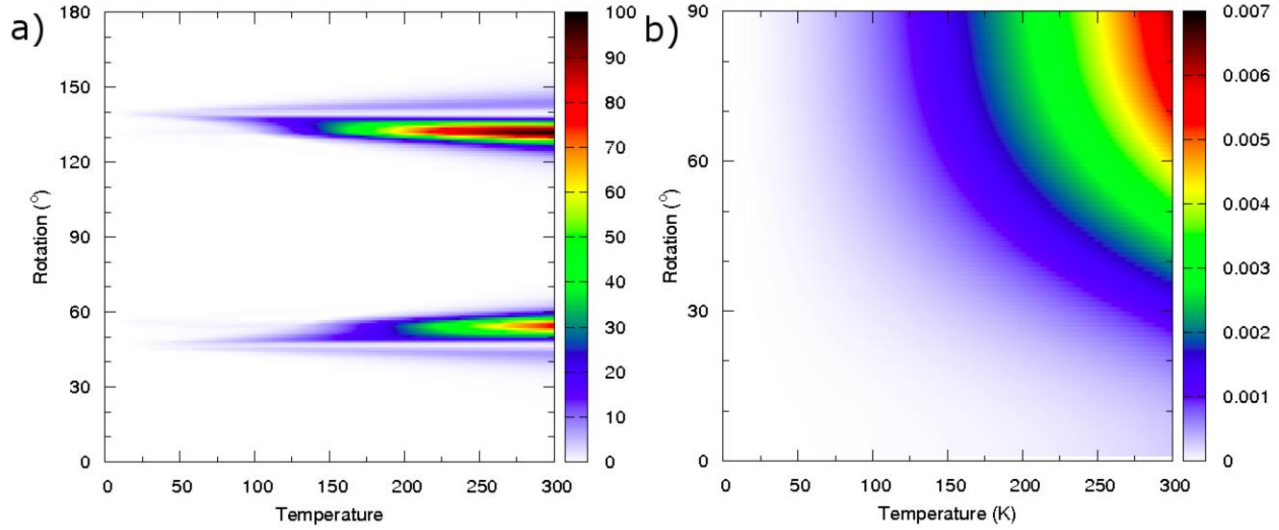
Rotation-induced movement of the resonances and antiresonances





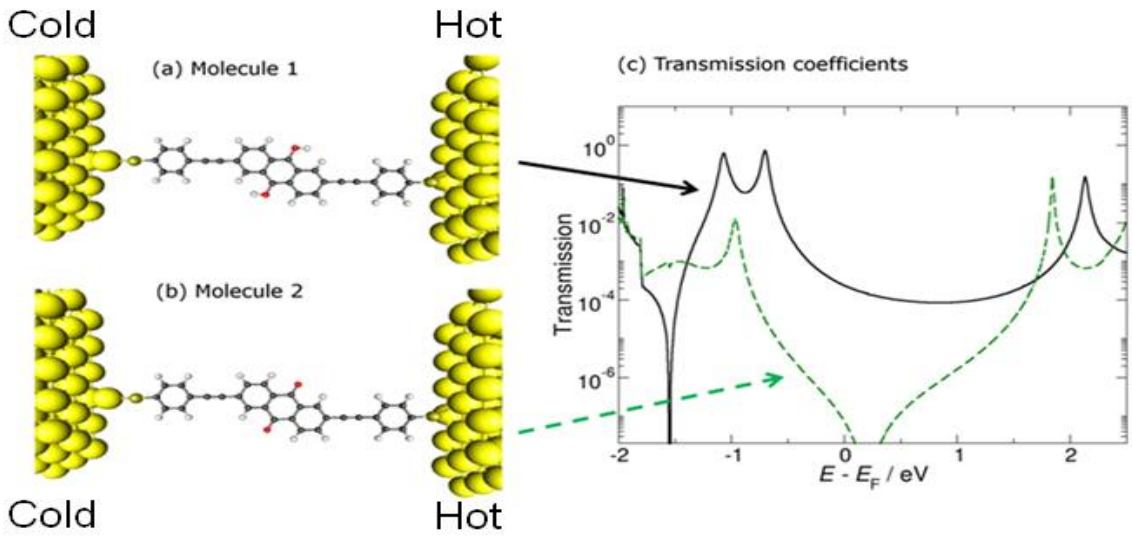
- Thermopower and figure of merit



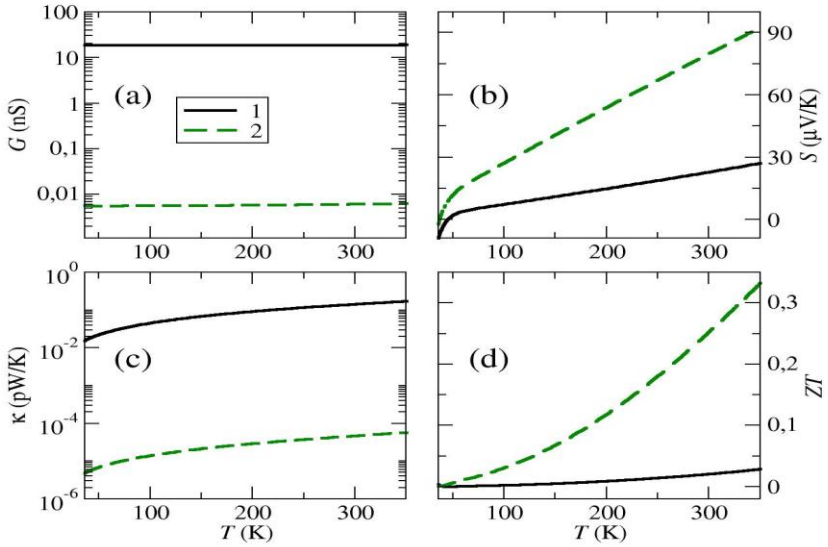


Huge enhancement due to the Fano resonance in the first case

- OPE molecules. MP interference



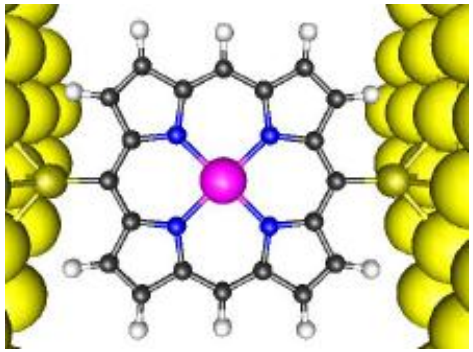
On-site energy-induced movement of the antiresonance



Reduction of G and κ. Enhancement of S and ZT

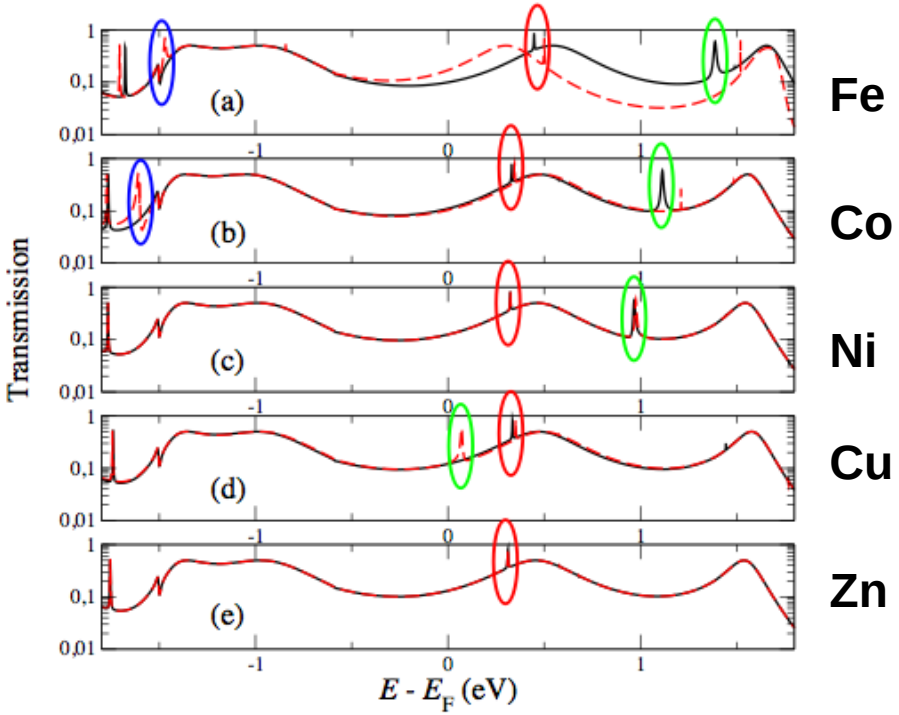
3) Symmetry-induced thermoelectric effects

- System: magnetic molecule couple to metallic leads



Metalloporphyrin molecule coupled via sulfur contacts to gold leads

Metal = Fe, Co, Ni, Cu or Zn



Fe

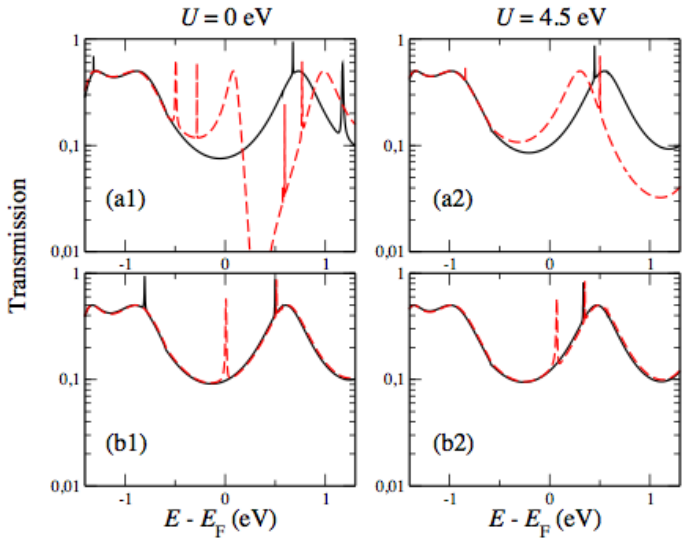
Co

Ni

Cu

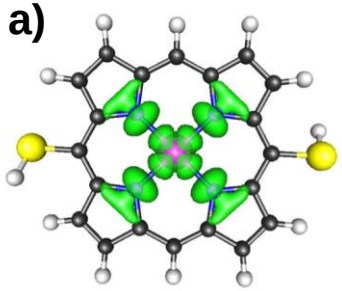
Zn

Effect of Coulomb repulsion



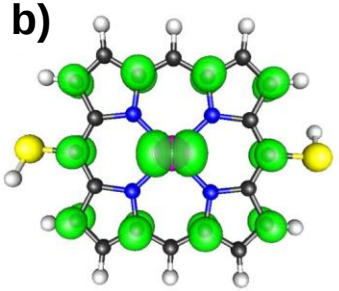
- Symmetry-dependent molecular orbitals

a)



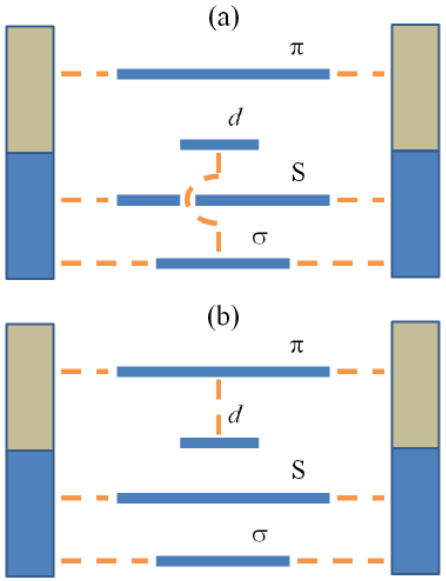
d **state coupled to σ orbitals**

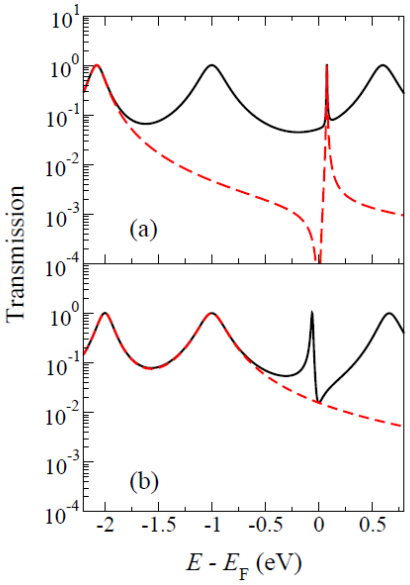
b)



d **state coupled to π orbitals**

Model: four levels coupled to featureless leads



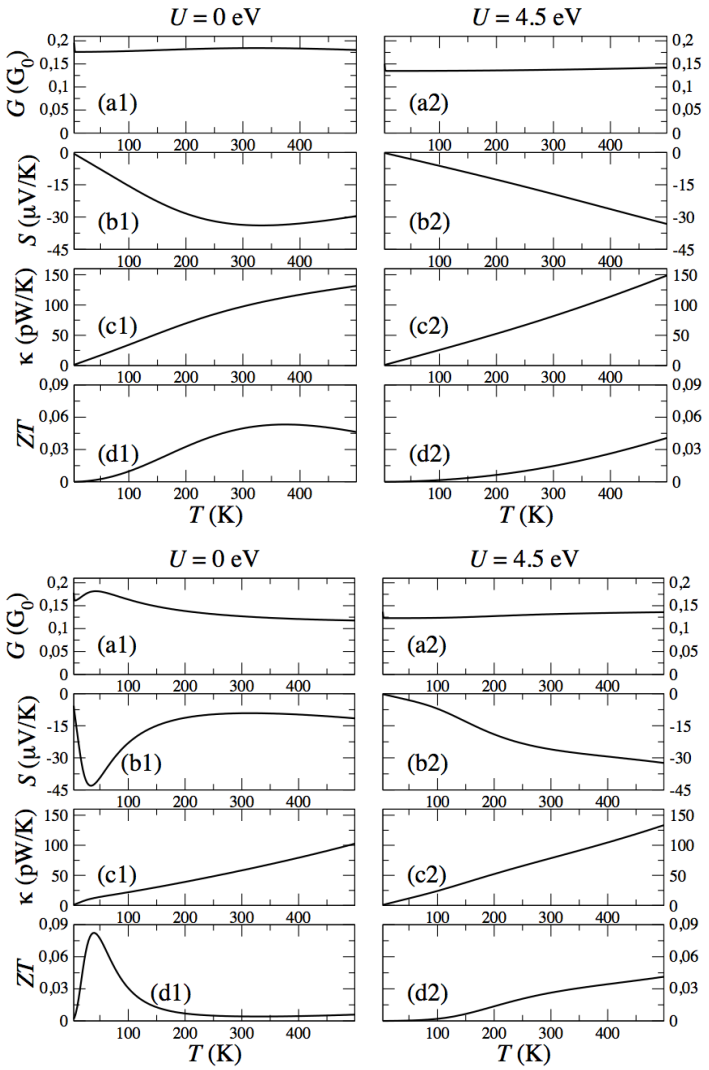


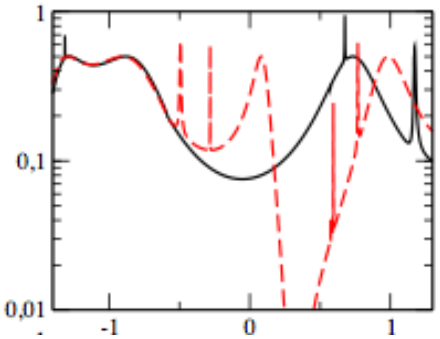
BW

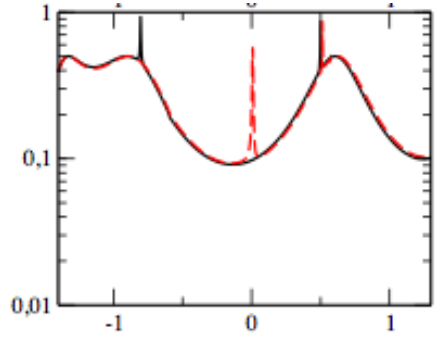
Fano

Symmetry-induced Fano resonances

- Thermoelectric properties as a function of temperature for the Fe metalloporphyrin

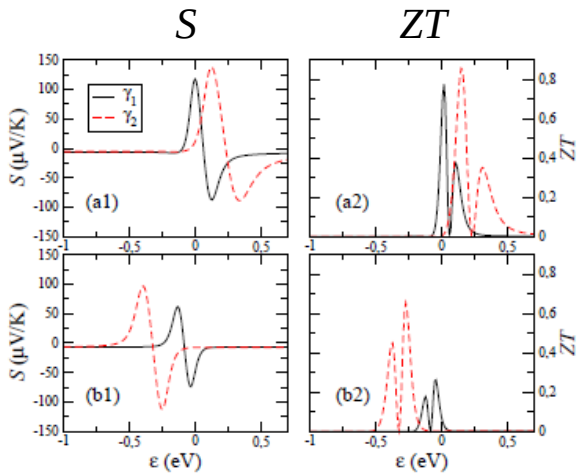






Thermoelectric properties as a function of temperature

- Thermoelectric properties as a function of the position of the *d* state and its coupling to the rest of the molecule (γ)

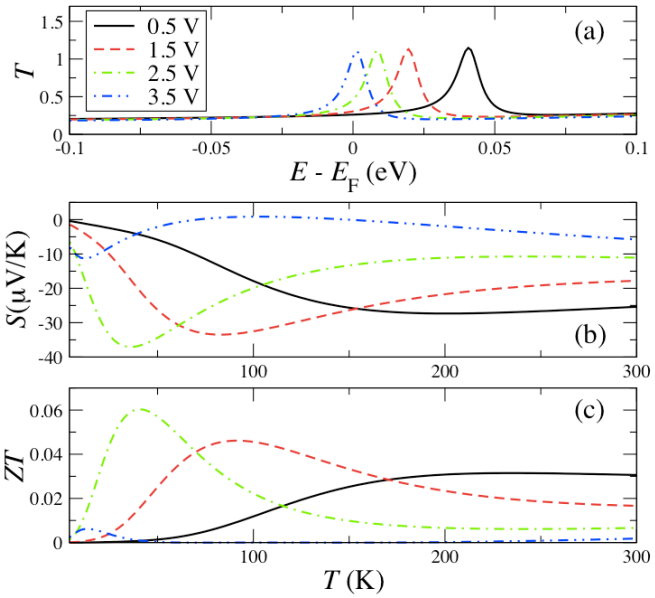


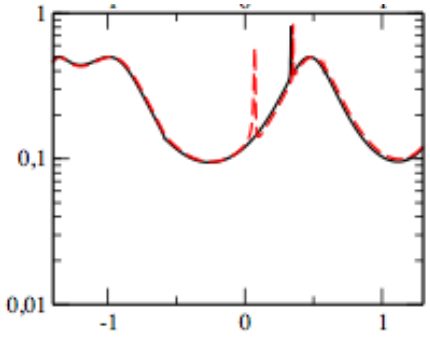
BW $T = 250\,\mathrm{K}$

$\gamma_1 = 0.2$

Fano $\gamma_2 = 0.4$

Changes in width and position of features

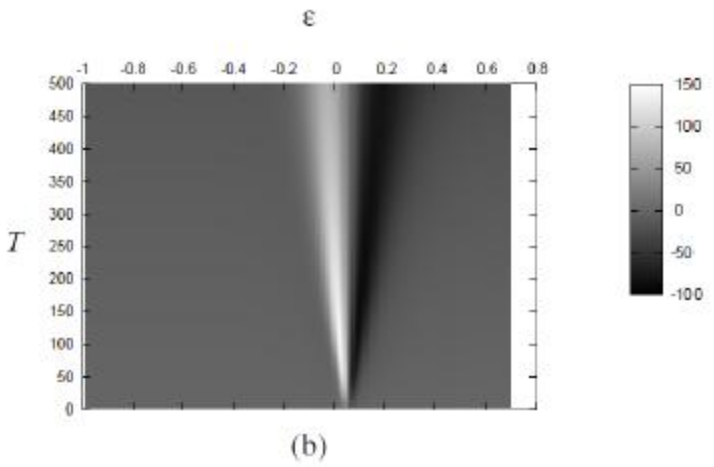


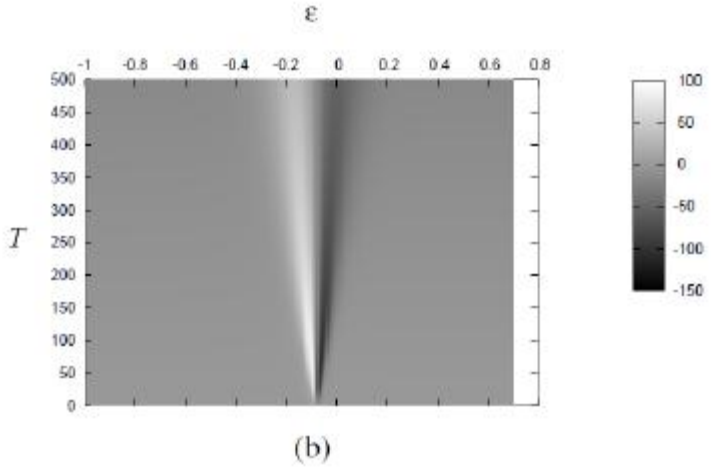


Cu metalloporphyrin

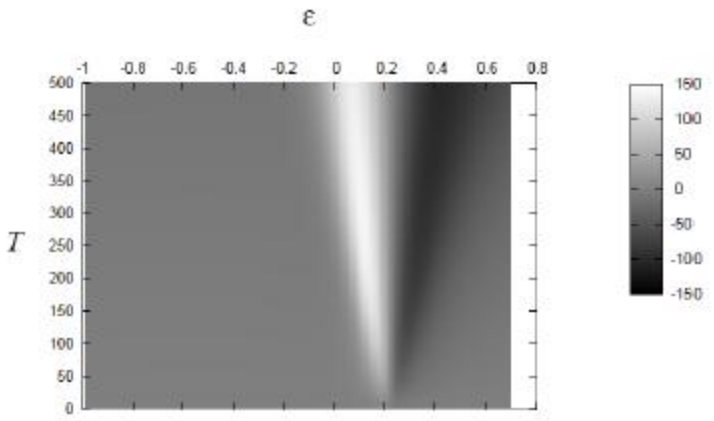
- Temperature dependence of S

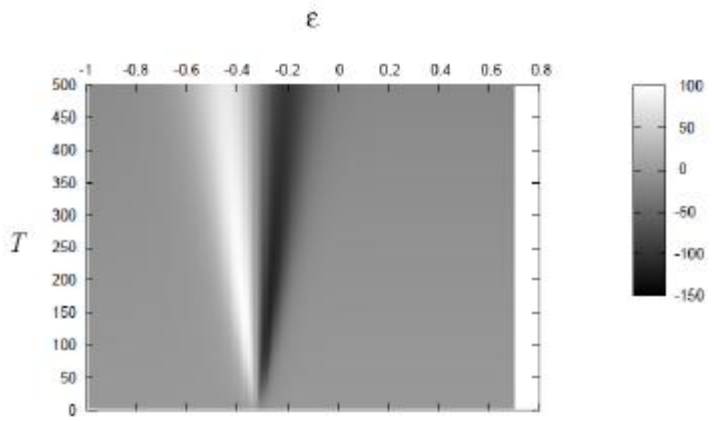
BW **Fano**





$\gamma_1 = 0.2$

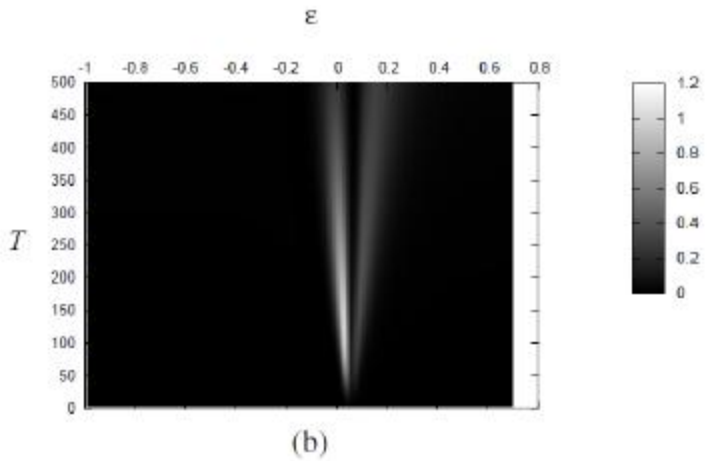


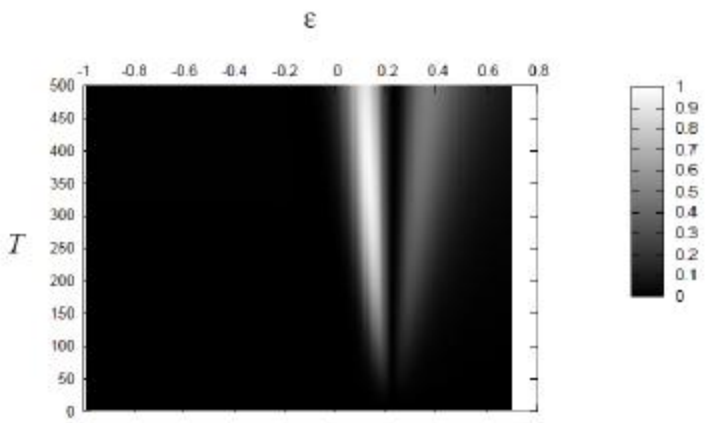


$\gamma_2 = 0.4$

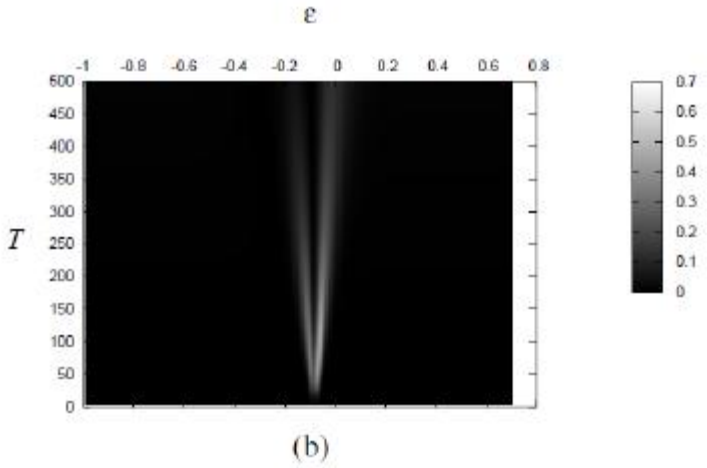
- Temperature dependence of ZT

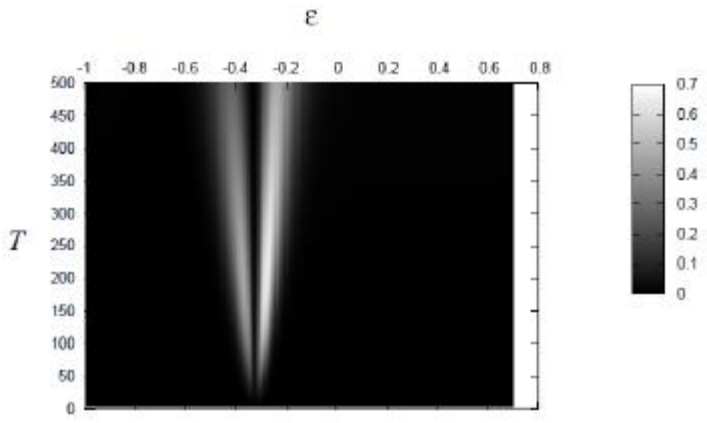
BW





Fano





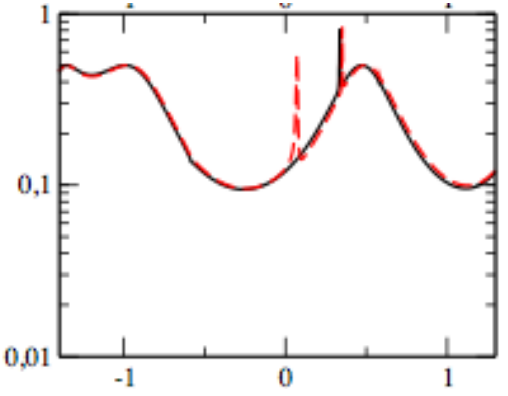
$\gamma_1 = 0.2$

$\gamma_2 = 0.4$

- Spin-dependent thermoelectric coefficients

$$\begin{pmatrix} I \\ \dot{Q} \end{pmatrix} = \frac{1}{h} \begin{pmatrix} e^2(L_0^{\uparrow} + L_0^{\downarrow}) & (e/T)(L_1^{\uparrow} + L_1^{\downarrow}) \\ e(L_1^{\uparrow} + L_1^{\downarrow}) & (1/T)(L_2^{\uparrow} + L_2^{\downarrow}) \end{pmatrix} \begin{pmatrix} \Delta V \\ \Delta T \end{pmatrix}$$

$$L_n^{\sigma} = \int_{-\infty}^{\infty} (E - E_F)^n T^{\sigma}(E) \frac{\partial f(E,V,T)}{\partial E} \mathrm{d}E$$

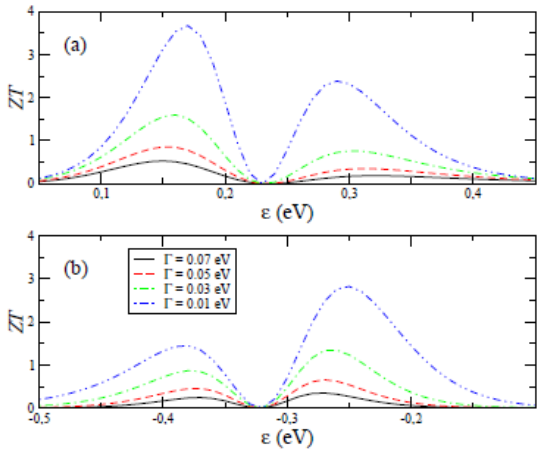


$$G = \frac{e^2}{h}(L_0^{\uparrow} + L_0^{\downarrow}) \qquad S = \frac{-1}{eT} \frac{L_1^{\uparrow} + L_1^{\downarrow}}{L_0^{\uparrow} + L_0^{\downarrow}} \qquad \Pi = \frac{1}{e} \frac{L_1^{\uparrow} + L_1^{\downarrow}}{L_0^{\uparrow} + L_0^{\downarrow}} \qquad \kappa = \frac{1}{hT} \left(L_2^{\uparrow} + L_2^{\downarrow} - \frac{(L_1^{\uparrow} + L_1^{\downarrow})^2}{L_0^{\uparrow} + L_0^{\downarrow}} \right)$$

$$ZT = \frac{1}{\dfrac{(L_0^{\uparrow} + L_0^{\downarrow})(L_2^{\uparrow} + L_2^{\downarrow})}{(L_1^{\uparrow} + L_1^{\downarrow})^2} - 1}$$

One of the spin components can mask the effect of the other

- Effect of the coupling to the electrodes

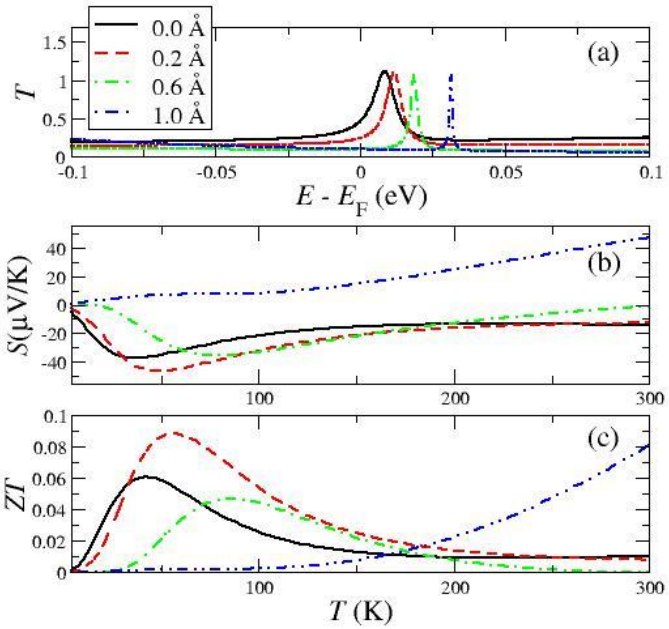


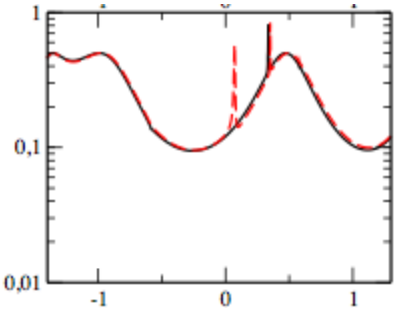
BW

Fano

$T = 250\,\mathrm{K}$

The smaller Γ, the larger the ZT maxima





Cu metalloporphyrin

Conclusions

- Largest thermopower and ZT produced by multiple-path interference effects

- Qualitative details of the figure of merit depend on molecular intrinsic properties

- The highest value of the figure of merit is determined by the coupling strength

Thank you