

# Quantum interference effects in electron transport: How to select suitable molecules for logic gates and thermoelectric devices



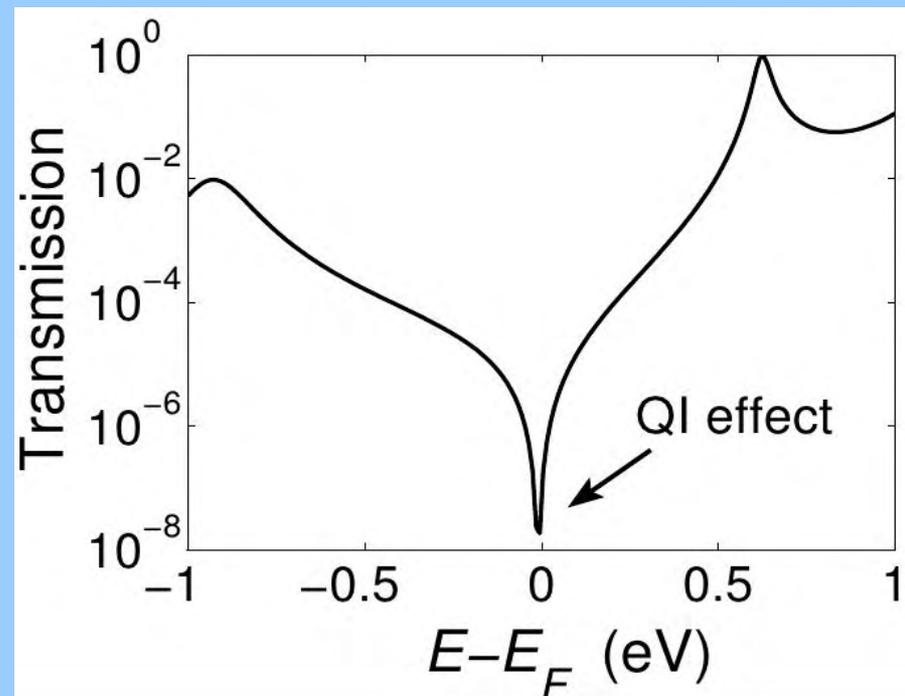
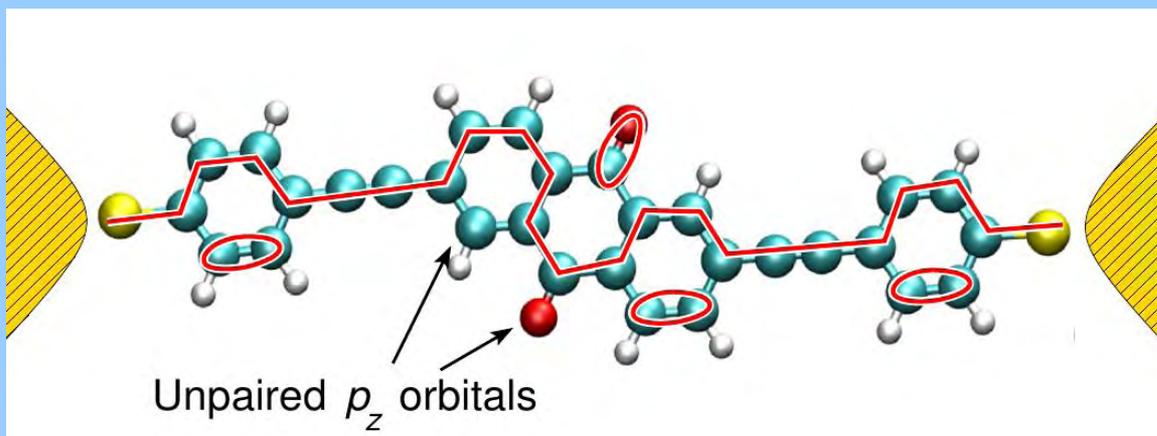
**Robert Stadler**

University of Vienna

Department of Physical Chemistry



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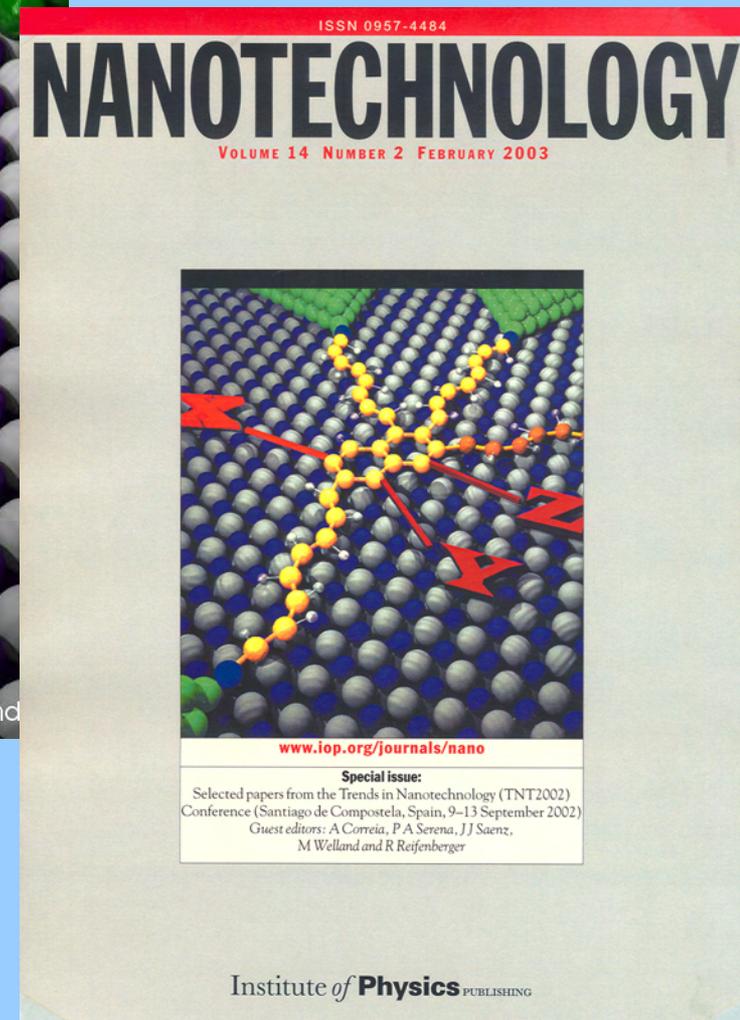
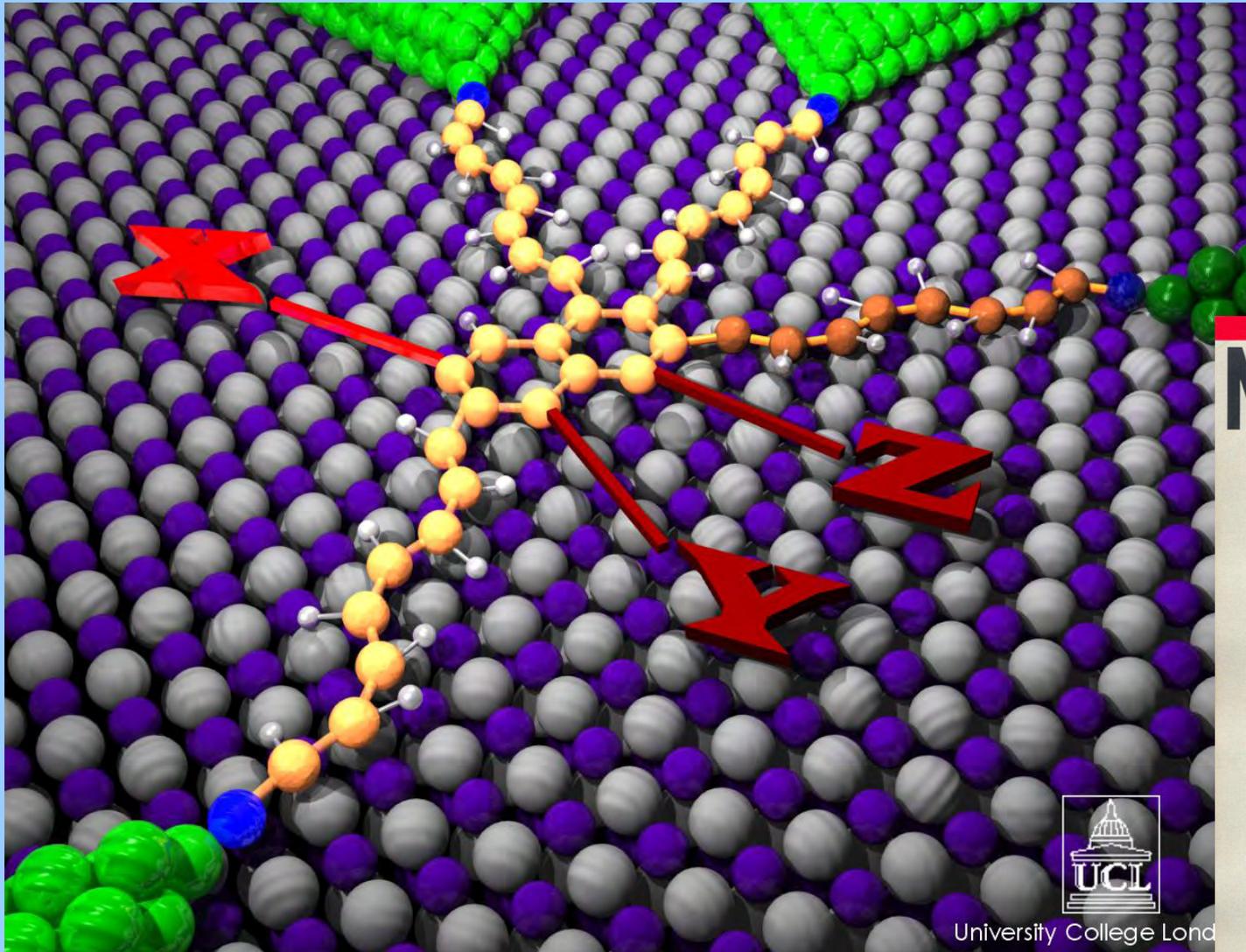


**Troels Markussen and  
Kristian S. Thygesen**  
Technical University of Denmark  
Department of Physics

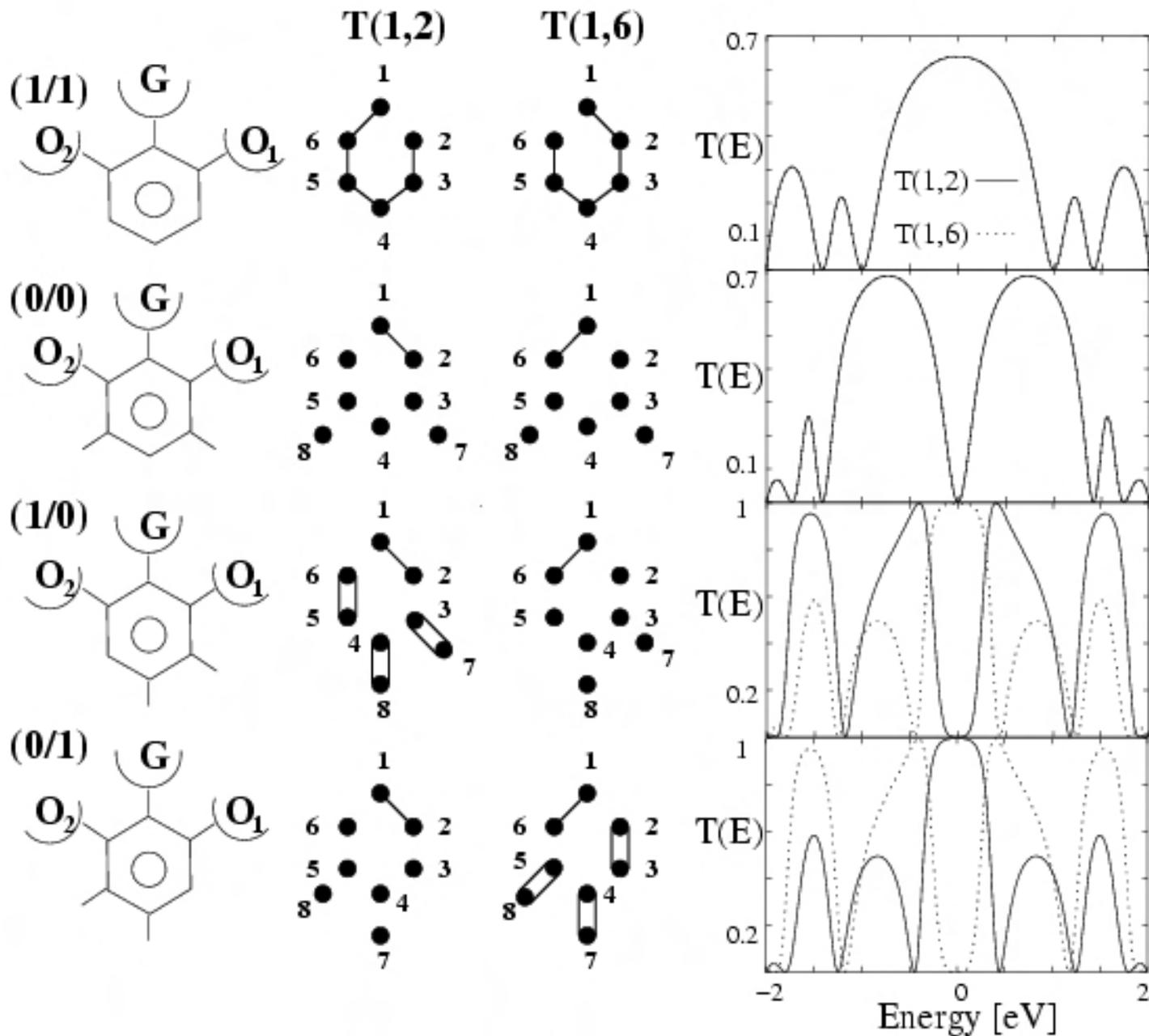


# QIE for devices

R. Stadler, M. Forshaw and C. Joachim  
Nanotechnology **14** (2003) 138



# Graphical rules – Device design (1)



IST-1999-11565

In a first evaluation of the vision on a tight binding-scattering theory level a **proof of concept** was achieved.



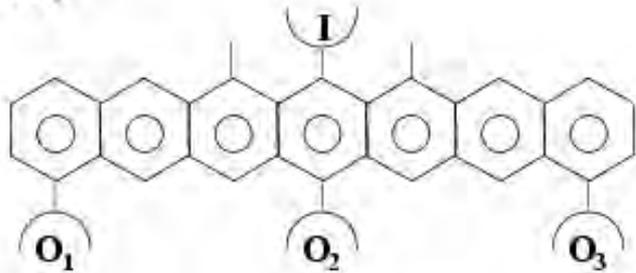
**BUN**  
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Nanomachines

# Graphical rules – Device design (2)

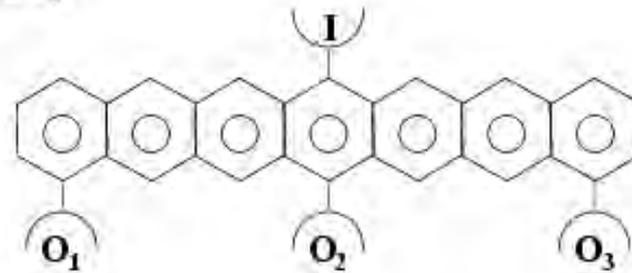


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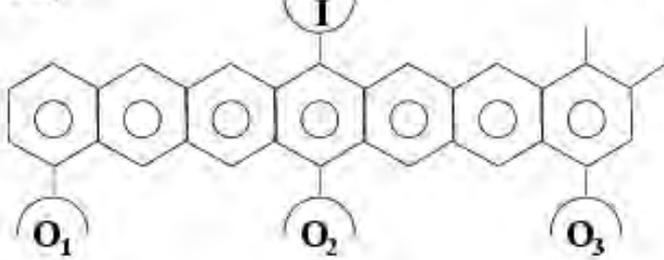
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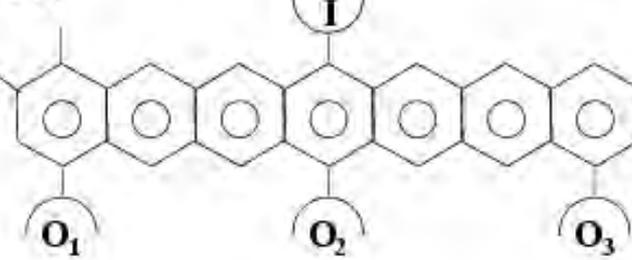
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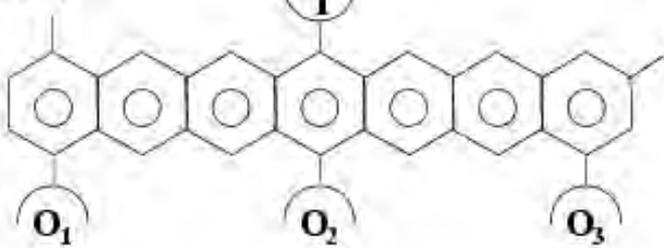
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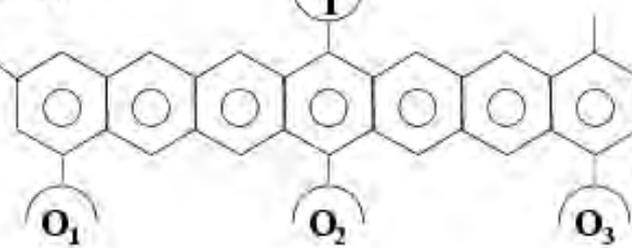
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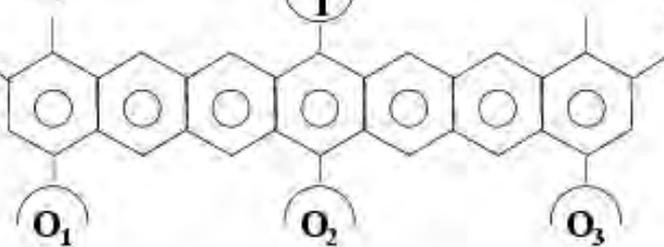
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(001)



(010)



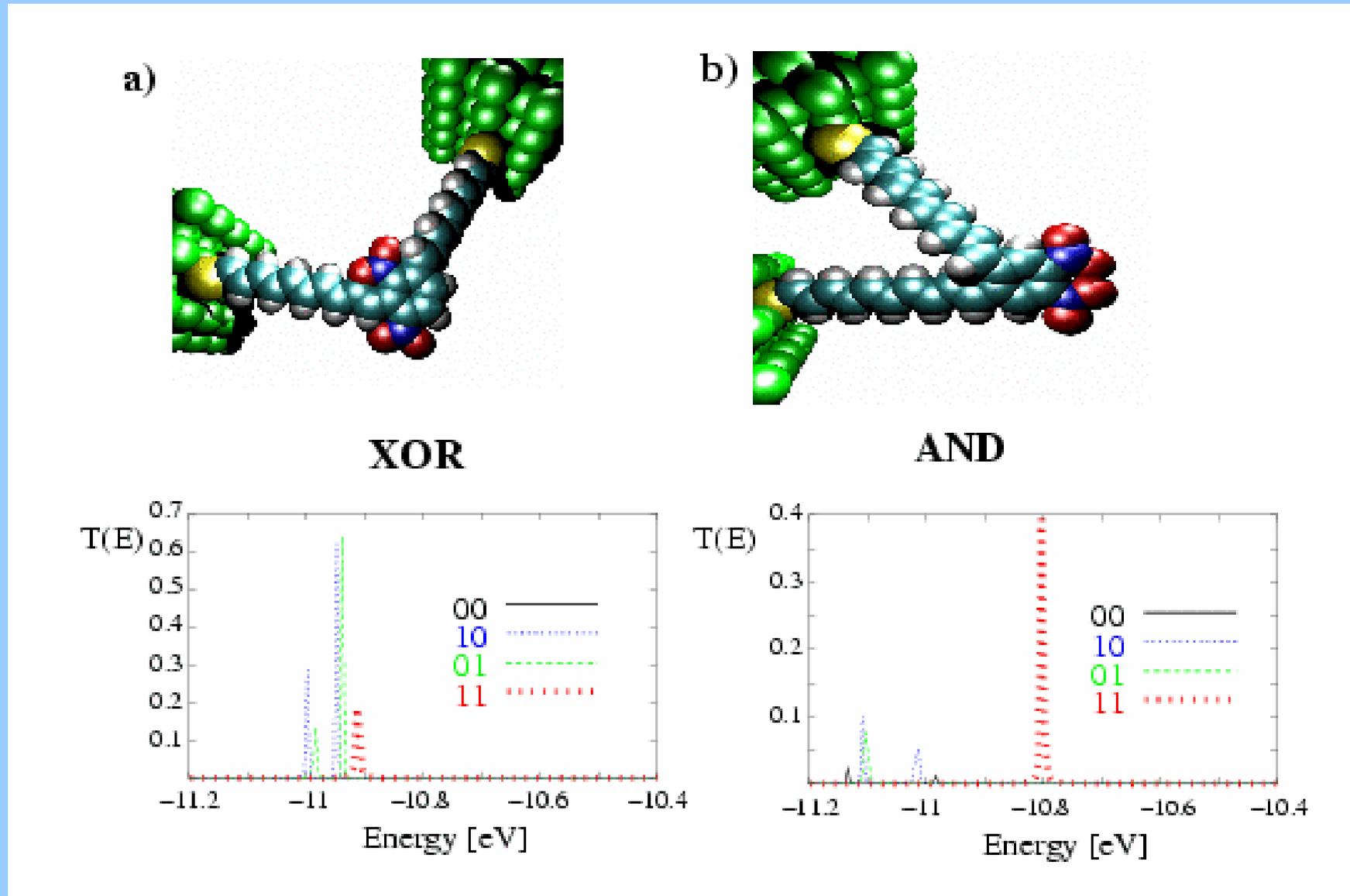
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# Integrating logic functions inside a single molecule

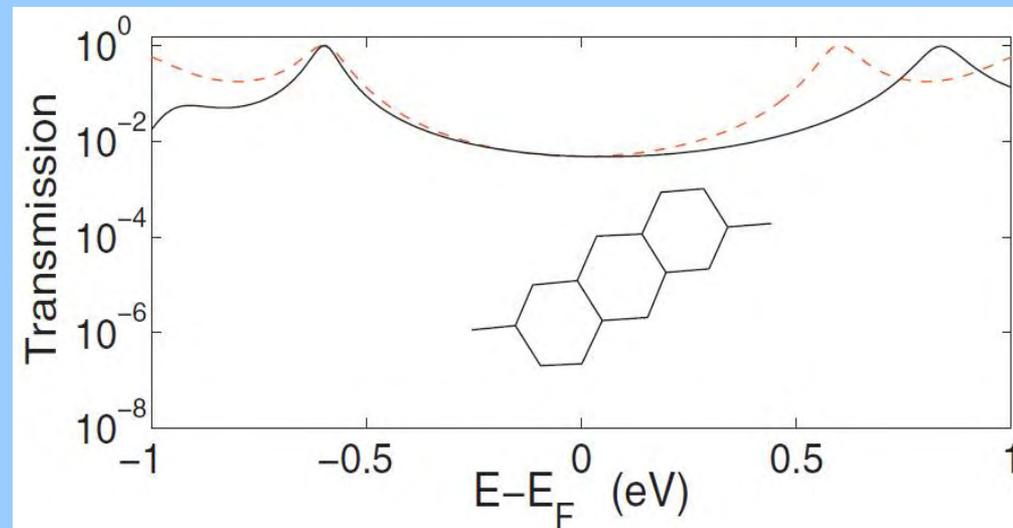
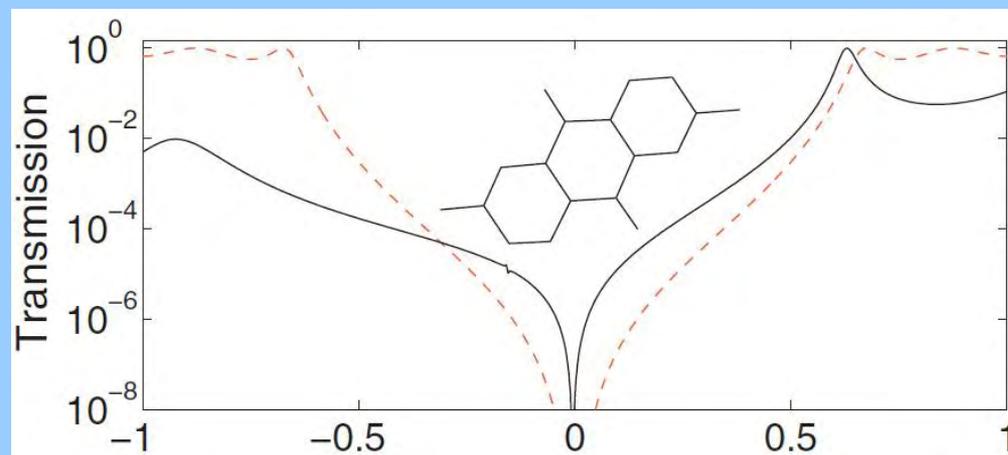
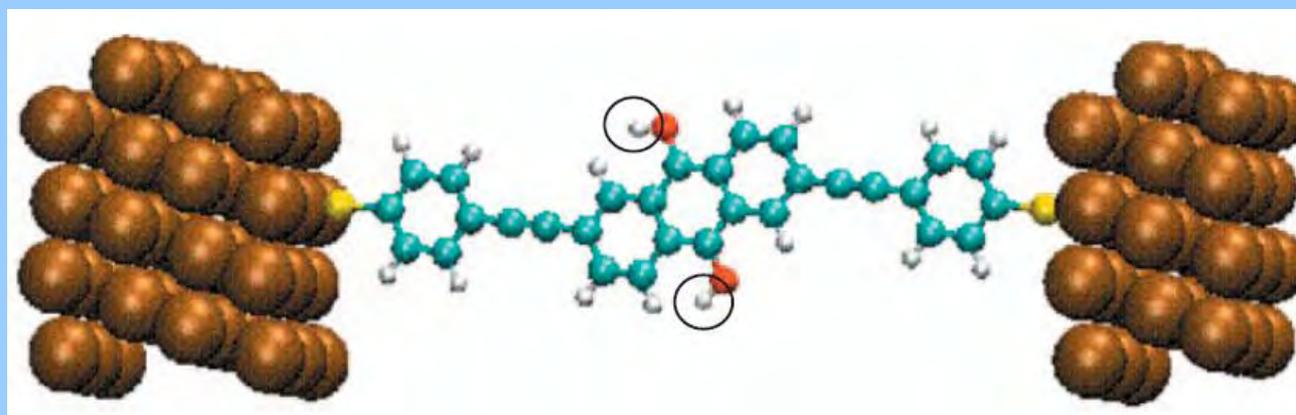


# Electrochemical control of quantum interference in anthraquinone-based molecular switches

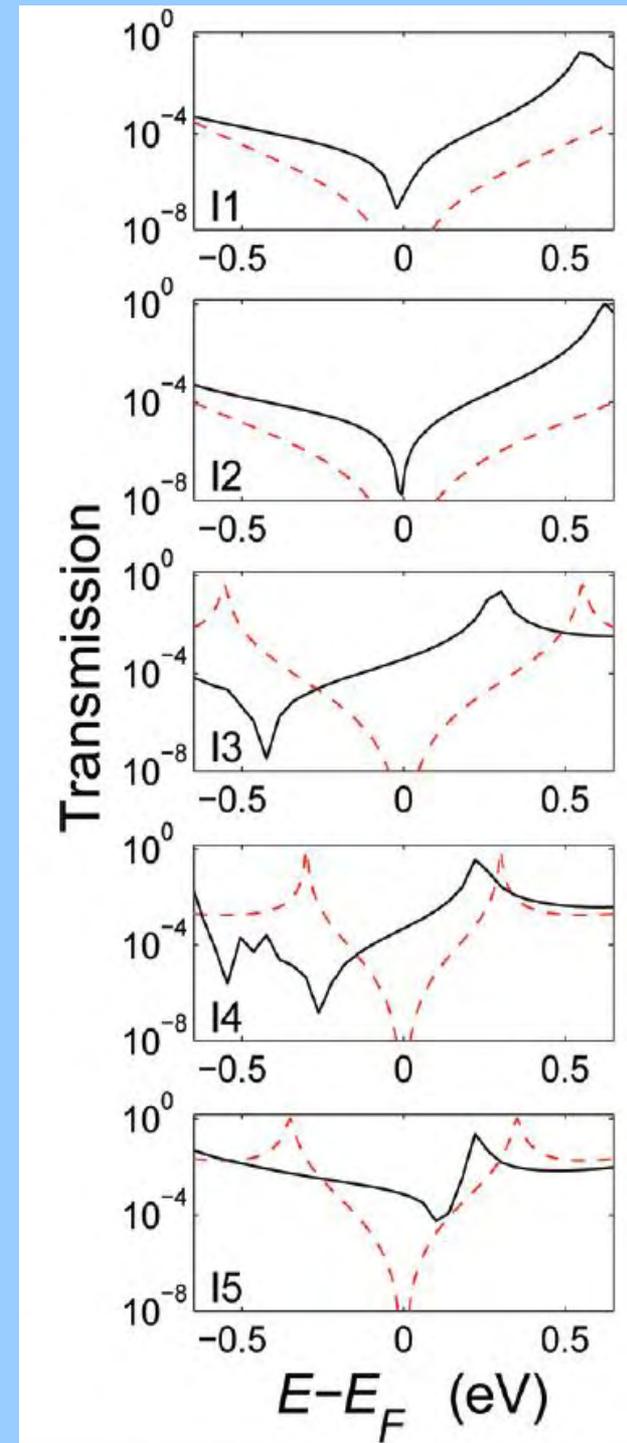
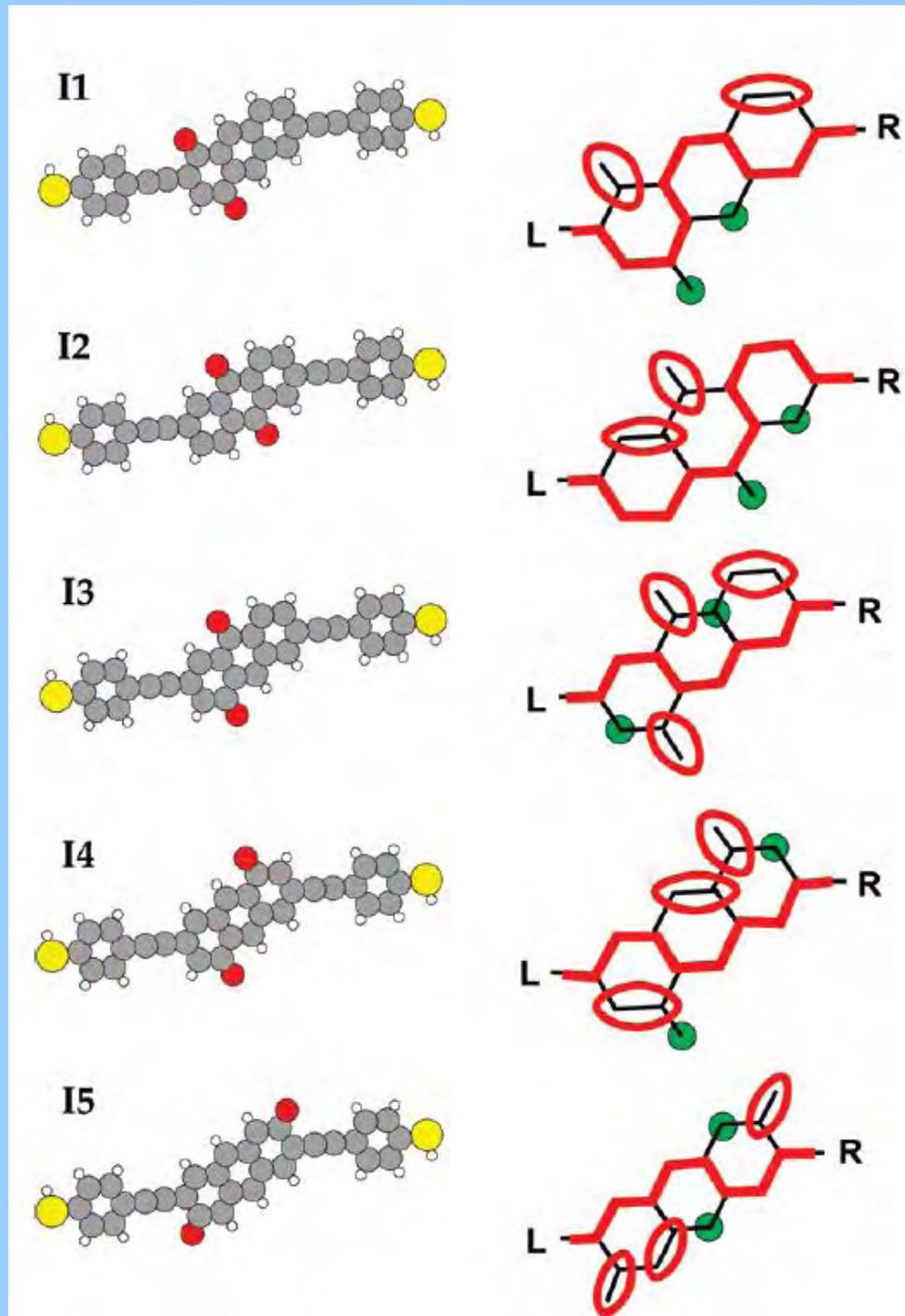
Troels Markussen,<sup>1,2,a)</sup> Jakob Schiötz,<sup>2</sup> and Kristian S. Thygesen<sup>1</sup>

<sup>1</sup>*Department of Physics, Center for Atomic-scale Materials Design (CAMD), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

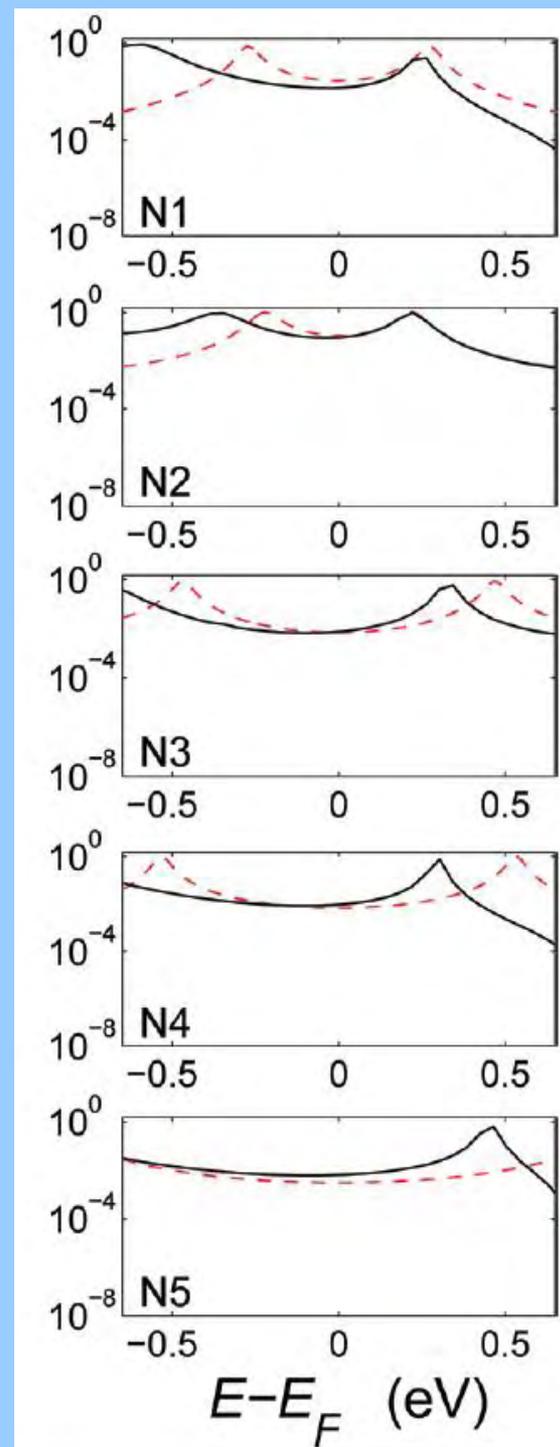
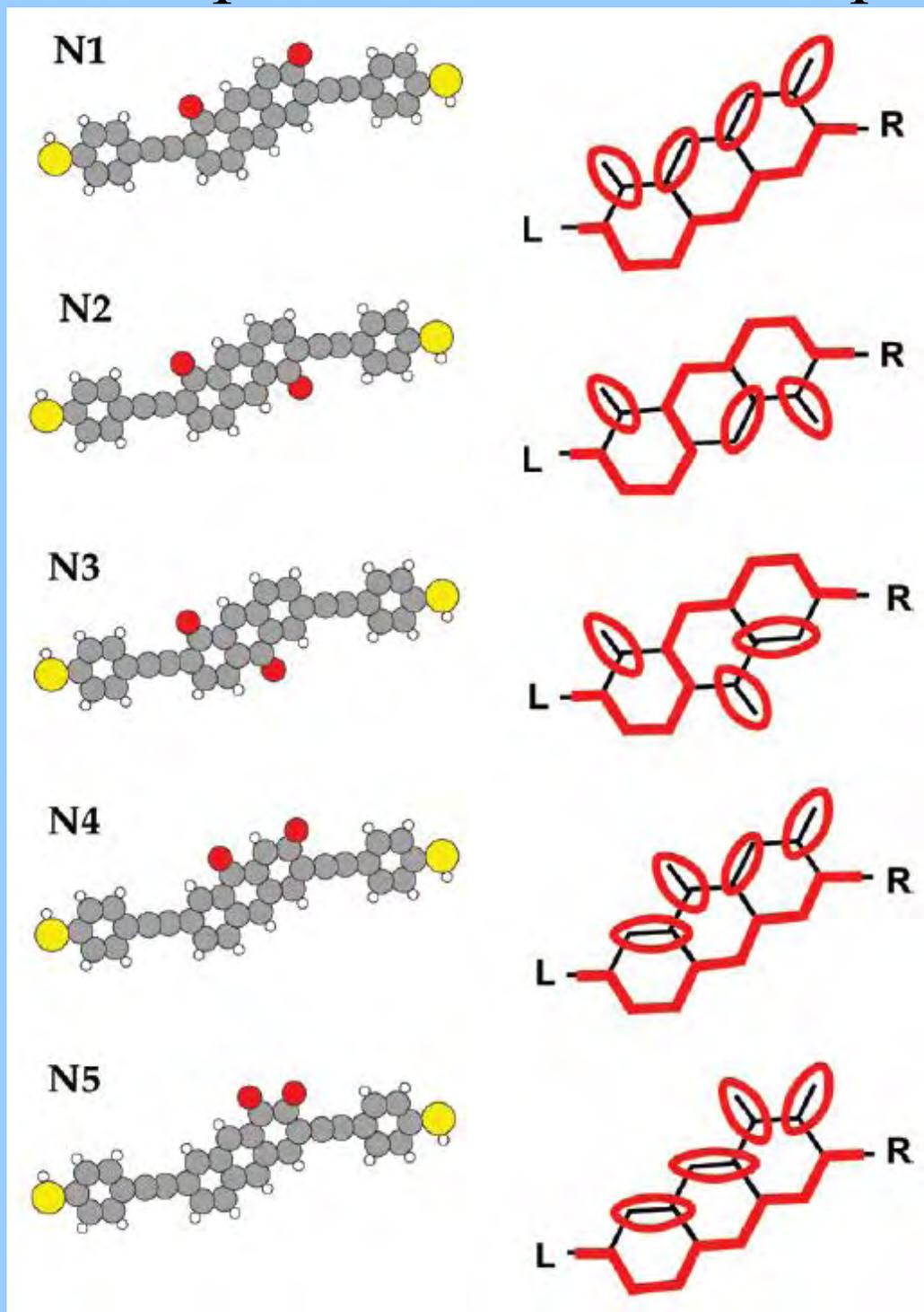
<sup>2</sup>*Department of Physics, Danish National Research Foundations, Center of Individual Nanoparticle Functionality (CINF), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*



# Graphical rules - anthraquinone configurations (1)



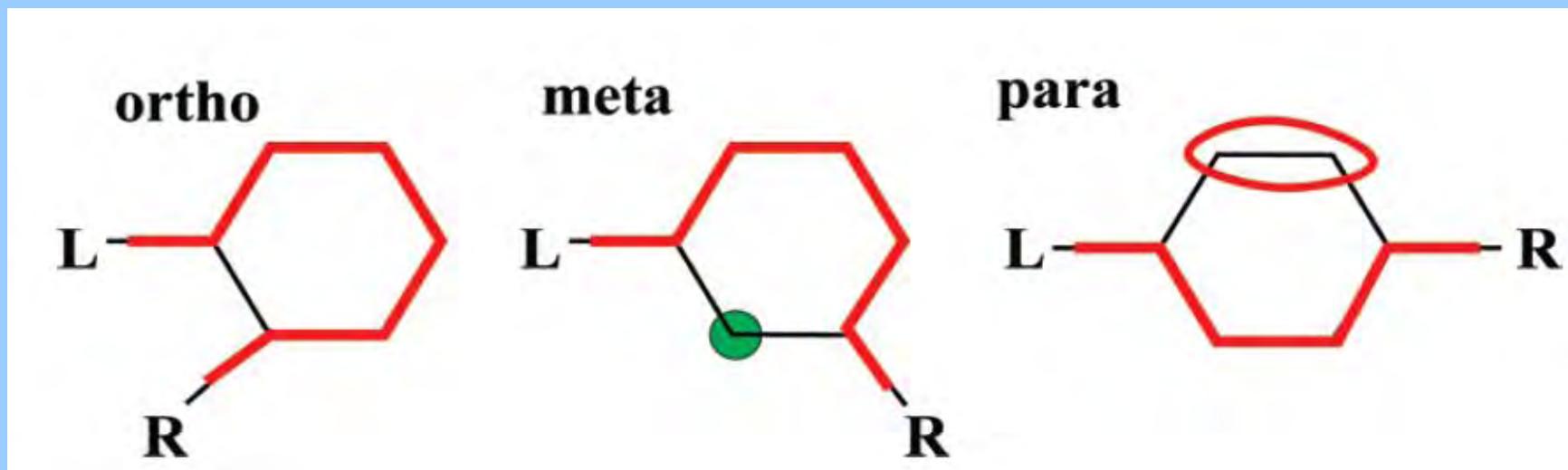
# Graphical rules - anthraquinone configurations (2)



# Graphical rules - anthraquinone configurations (3)

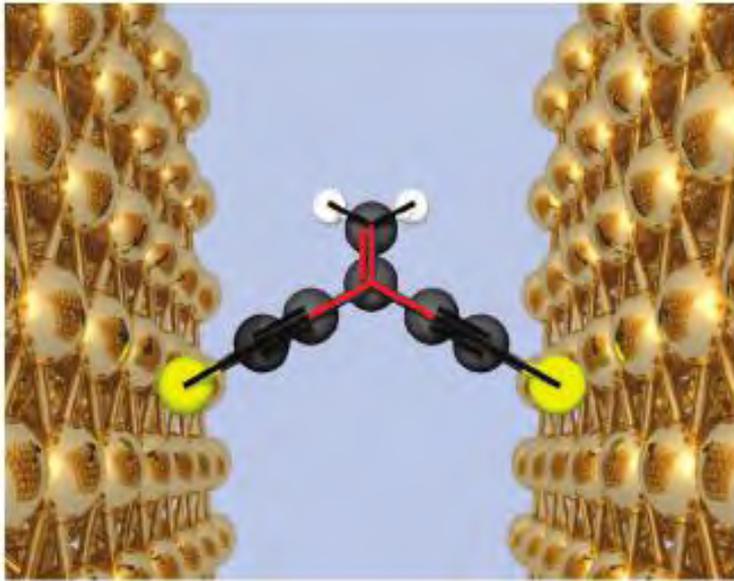
Molecule	$G (G_0)$	Molecule	$G (G_0)$
I1	$7.71 \cdot 10^{-8}$	N1	$1.38 \cdot 10^{-2}$
I2	$1.82 \cdot 10^{-8}$	N2	$8.57 \cdot 10^{-2}$
I3	$3.03 \cdot 10^{-4}$	N3	$7.09 \cdot 10^{-3}$
I4	$3.55 \cdot 10^{-4}$	N4	$8.98 \cdot 10^{-3}$
I5	$8.84 \cdot 10^{-4}$	N5	$6.19 \cdot 10^{-3}$

Graphical rules – benzene – ortho, meta, para

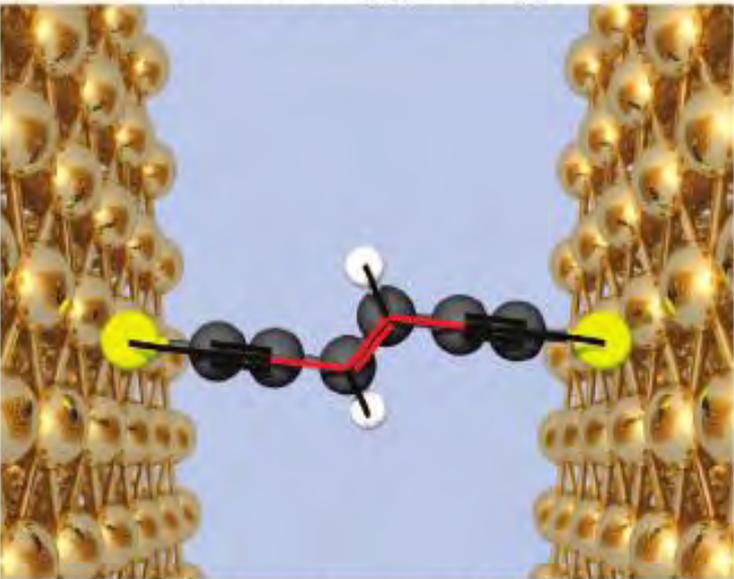


# Graphical rules – Cross-conjugated molecules

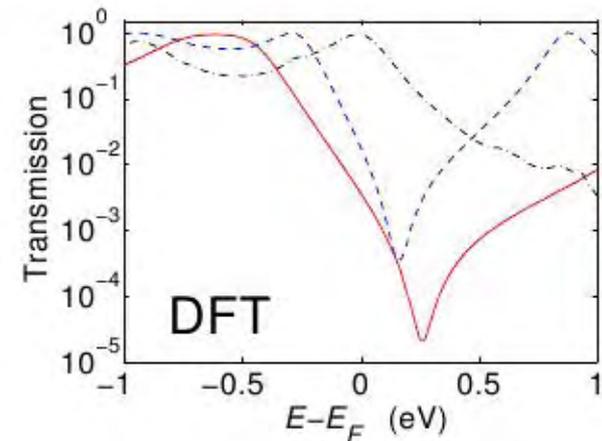
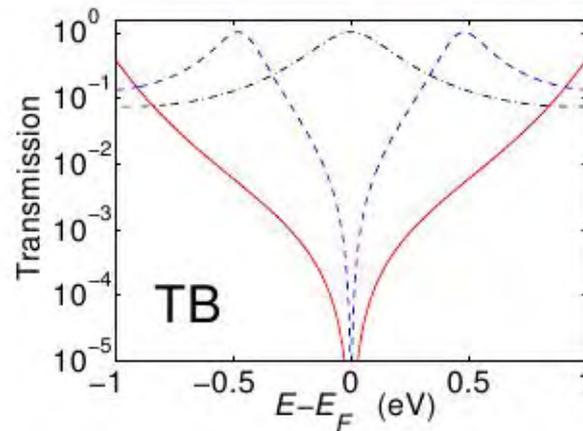
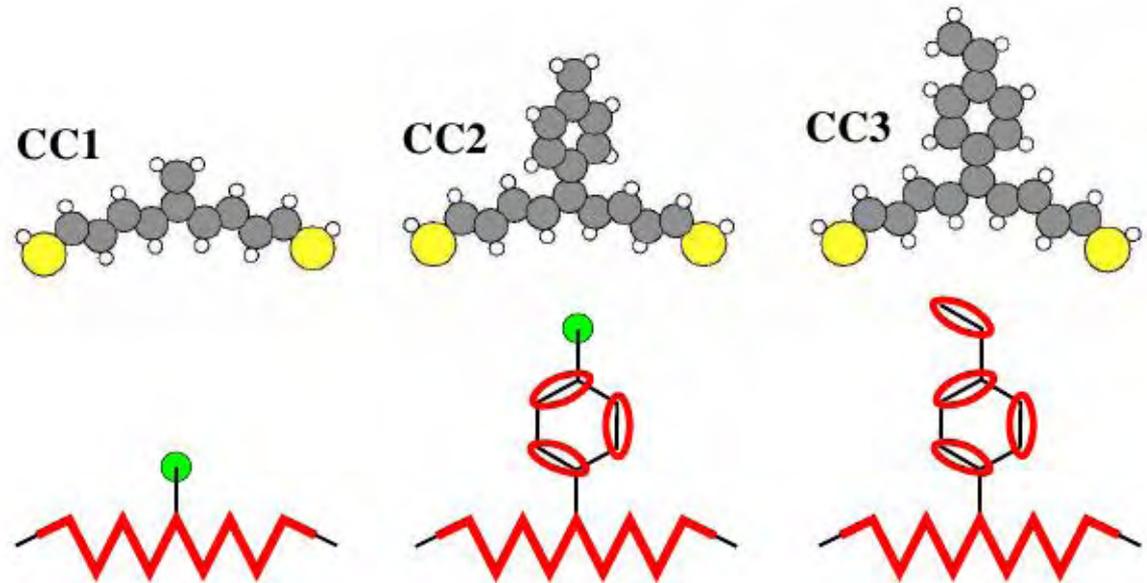
QI effects in cross-conjugated molecules have been investigated in a series of recent papers by Gemma Solomon, Mark Ratner and co-workers.



(a) A cross-conjugated bridge.



(b) A linearly conjugated bridge.



# Graphical rules – derivation within NEGF (1)

Within a single-particle picture, the transmission probability of an electron entering a molecular junction with an energy  $E$  is given by<sup>38</sup>

$$T(E) = \text{Tr}[G\Gamma_L G^\dagger \Gamma_R](E) \quad (1)$$

where  $G = (E - H_{\text{mol}} - \Sigma_L - \Sigma_R)^{-1}$  is the Green function matrix of the contacted molecule,  $\Sigma_{L/R}$  is the self-energy matrix due to the left/right lead, and  $\Gamma_{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^\dagger)$ . Let us assume that the Hamiltonian describing the molecule is given in terms of a basis consisting of localized atomic-like orbitals,  $\phi_1, \phi_2, \dots, \phi_N$ , and that only the two orbitals  $\phi_1$  and  $\phi_N$  couple to the left and right leads, respectively. In this case the transmission reduces to

$$T(E) = \gamma(E)^2 |G_{1N}(E)|^2, \quad (2)$$

where  $G_{1N}(E)$  is the (1N) matrix element of the Green function,  $G$ , and  $\gamma(E) = [\Gamma_L(E)]_{11} = [\Gamma_R(E)]_{NN}$ , where we have assumed identical coupling strengths to the left and right leads for

# Graphical rules – derivation within NEGF (2)

simplicity. The coupling strength,  $\gamma(E)$ , is related to the electronic structure of the electrode and the overlap between molecular orbitals and electrode wavefunctions. On the other hand, the QI effects are contained in  $G_{1N}(E)$ . The latter can be calculated using Cramer's rule

$$G_{1N}(E) = \frac{\det_{1N}(E - H_{\text{mol}})}{\det(E - H_{\text{mol}} - \Sigma_L - \Sigma_R)} \quad (3)$$

where  $\det_{1N}(E - H_{\text{mol}})$  is the determinant of the matrix obtained by removing the 1st row and  $N$ th column from  $E - H_{\text{mol}}$  and multiplying it by  $(-1)^{1+N}$ . Taking the Fermi energy to be zero without loss of generality, we can then state the condition for complete destructive interference,

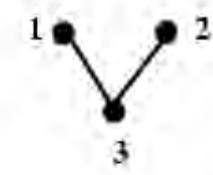
$$G(E_F) = 0, \text{ as}$$

$$\det_{1N}(H_{\text{mol}}) = 0.$$

(4)

# Graphical rules – topology and TB matrices (1)

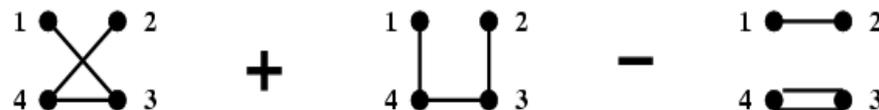
## 3 orbitals

$$M = \begin{bmatrix} -E & a_{12} & a_{13} \\ a_{12} & -E & a_{23} \\ a_{13} & a_{23} & -E \end{bmatrix}, \quad M_{12} = \begin{bmatrix} a_{12} & a_{23} \\ a_{13} & -E \end{bmatrix}, \quad c_0 = -a_{13} a_{23}$$


## 4 orbitals

$$M = \begin{bmatrix} -E & a_{12} & a_{13} & a_{14} \\ a_{12} & -E & a_{23} & a_{24} \\ a_{13} & a_{23} & -E & a_{34} \\ a_{14} & a_{24} & a_{34} & -E \end{bmatrix}, \quad M_{12} = \begin{bmatrix} a_{12} & a_{23} & a_{24} \\ a_{13} & -E & a_{34} \\ a_{14} & a_{34} & -E \end{bmatrix},$$

$$c_0 = a_{13} a_{23} a_{34} + a_{14} a_{23} a_{34} - a_{12} a_{34}^2$$



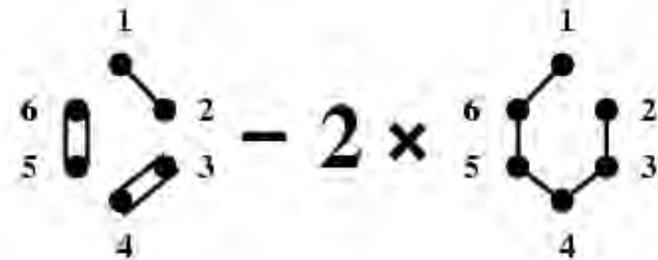
# Graphical rules – topology and TB matrices (2)

5 orbitals

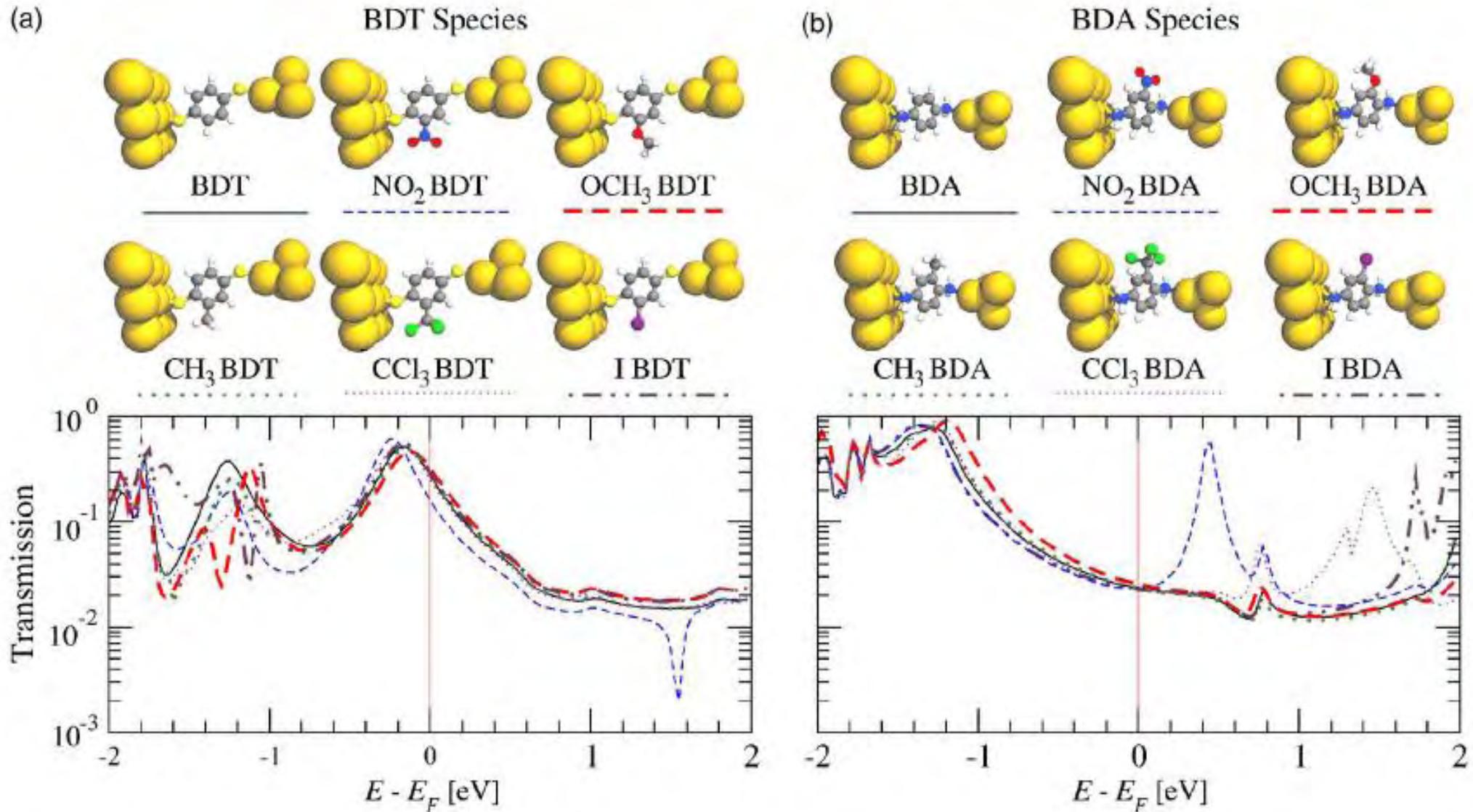
$$M = \begin{bmatrix} -E & a_{12} & a_{13} & a_{14} & a_{15} \\ a_{12} & -E & a_{23} & a_{24} & a_{25} \\ a_{13} & a_{23} & -E & a_{34} & a_{35} \\ a_{14} & a_{24} & a_{34} & -E & a_{45} \\ a_{15} & a_{25} & a_{35} & a_{45} & -E \end{bmatrix}, \quad M_{12} = \begin{bmatrix} a_{12} & a_{23} & a_{24} & a_{25} \\ a_{13} & -E & a_{34} & a_{35} \\ a_{13} & a_{34} & -E & a_{45} \\ a_{15} & a_{35} & a_{45} & -E \end{bmatrix}$$

$$c_0 = a_{34}^2 a_{15} a_{25} + a_{35}^2 a_{14} a_{24} + a_{45}^2 a_{13} a_{23} + 2 a_{12} a_{34} a_{35} a_{45} - a_{13} a_{24} a_{35} a_{45} - a_{14} a_{23} a_{35} a_{45} - a_{13} a_{25} a_{34} a_{45} - a_{15} a_{23} a_{34} a_{45} - a_{14} a_{25} a_{34} a_{35} - a_{15} a_{24} a_{34} a_{35}$$

A larger number of orbitals leads also to an increase in the number of possible paths. But the individual terms contain more couplings as well and if only one bond is missing, the path does not exist. Additionally, paths with opposite signs can cancel each other out. For 6 orbitals, there are 46 possible paths, but for e. g. benzene there are only 2:



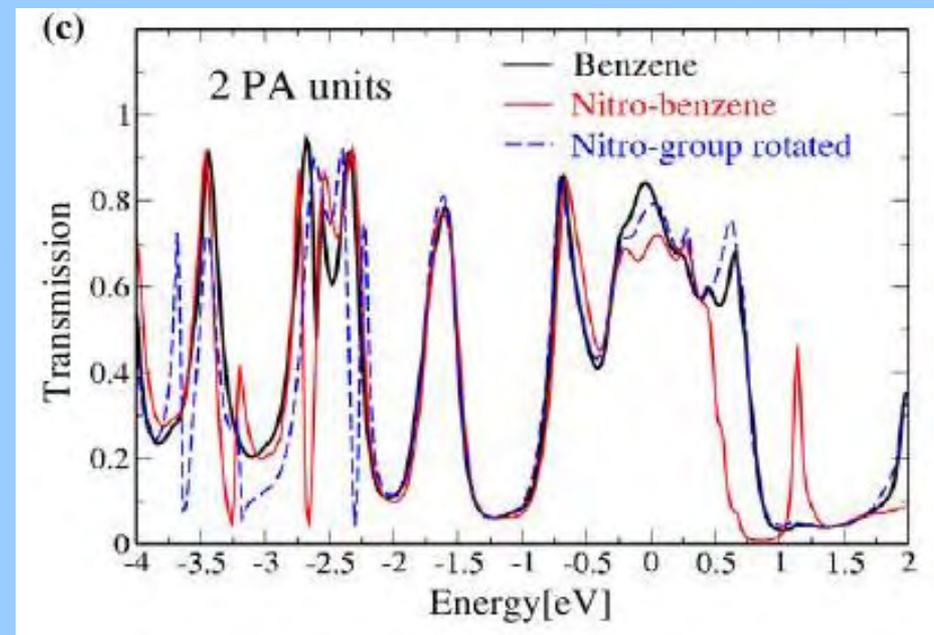
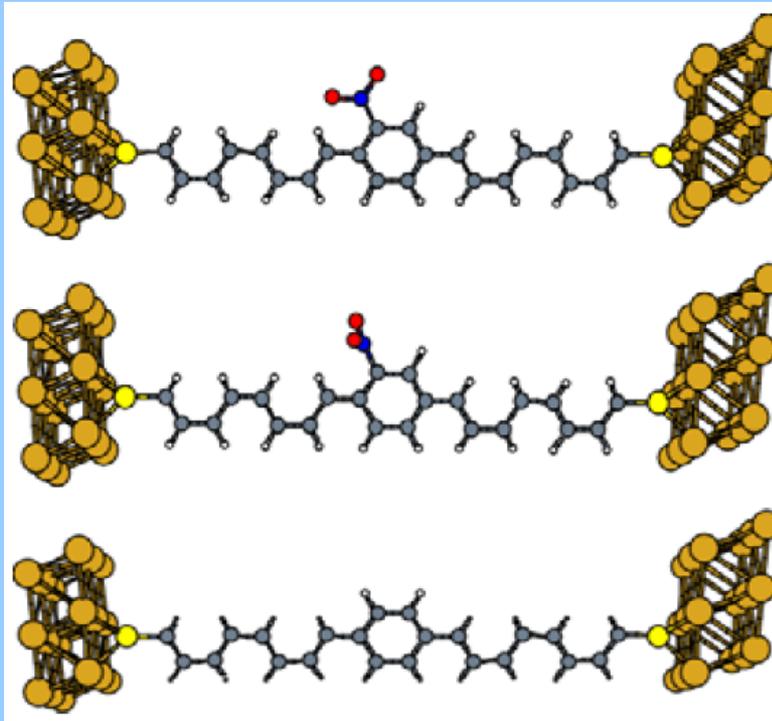
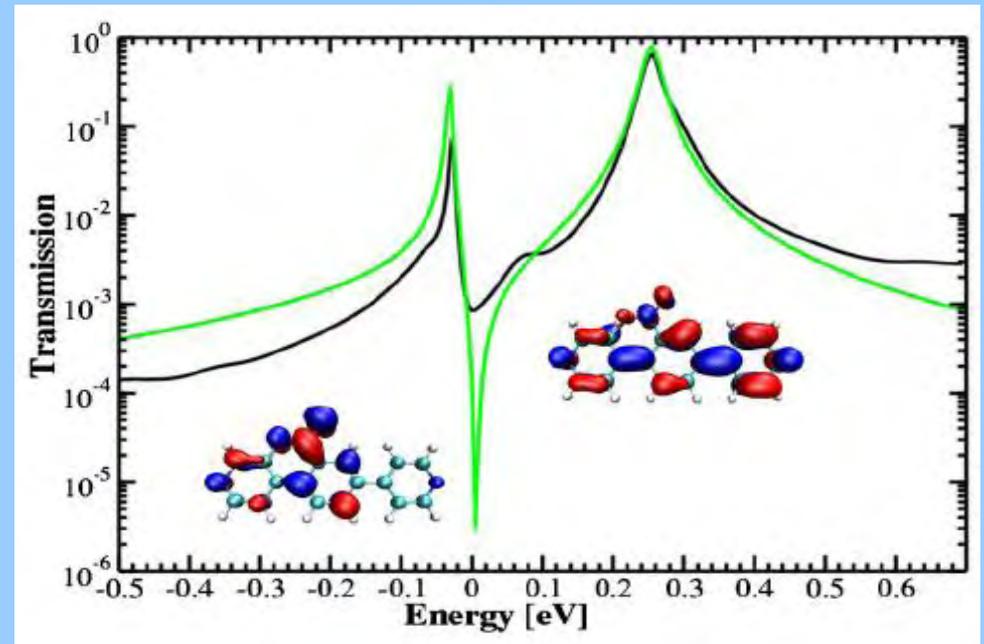
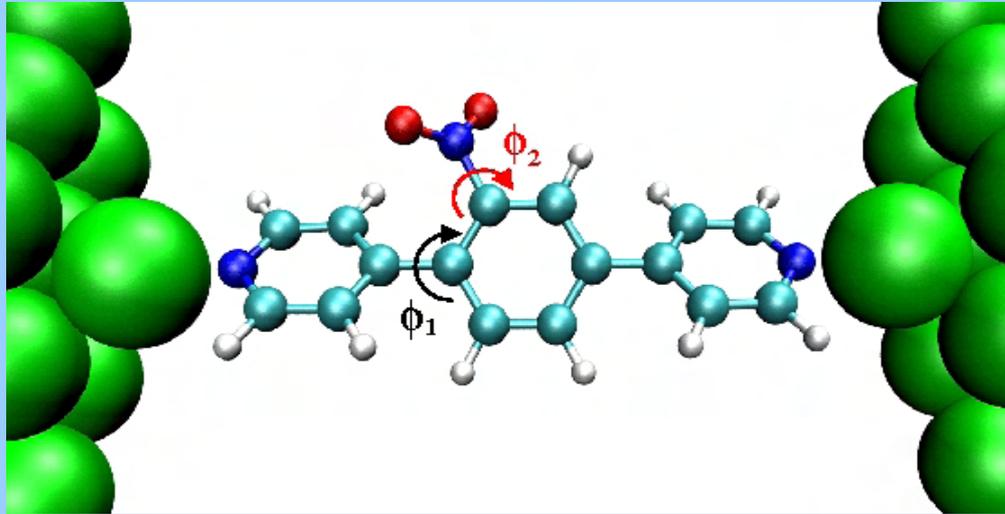
# Which side-groups can cause QIE? (1)



**D. J. Mowbray, G. Jones and K. S. Thygesen, JCP 128 (2008) 111103**

# Which side-groups can cause QIE? (2)

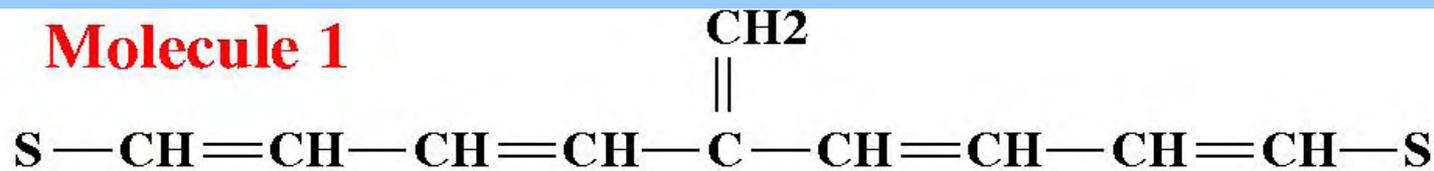
R. Stadler, PRB 80 (2009) 125401



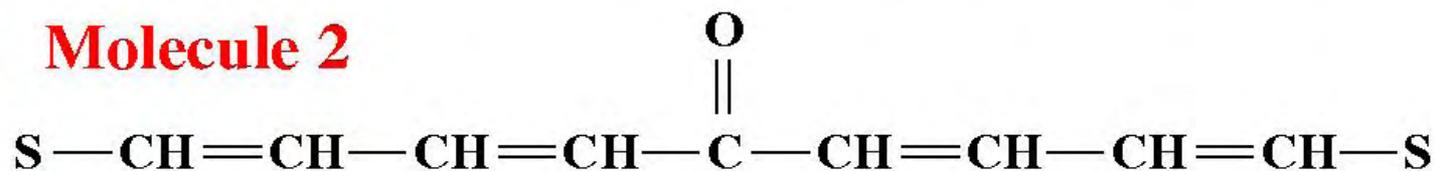
R. Stadler, K. S. Thygesen and K. W. Jacobsen, Nanotechnology 16 (2005) S155

# Which side-groups can cause QIE? (3)

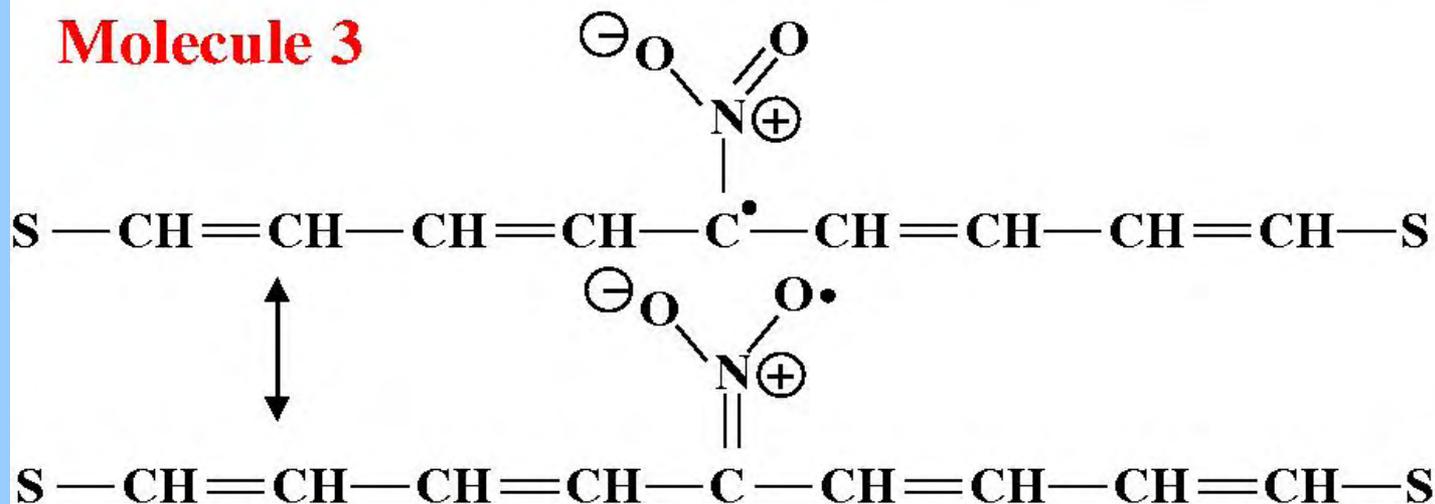
## Molecule 1



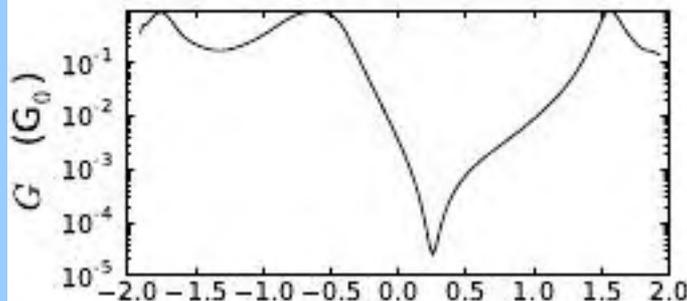
## Molecule 2



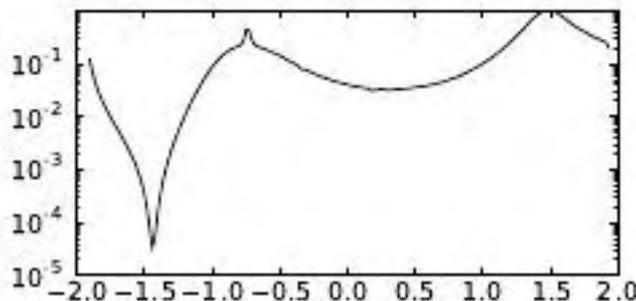
## Molecule 3



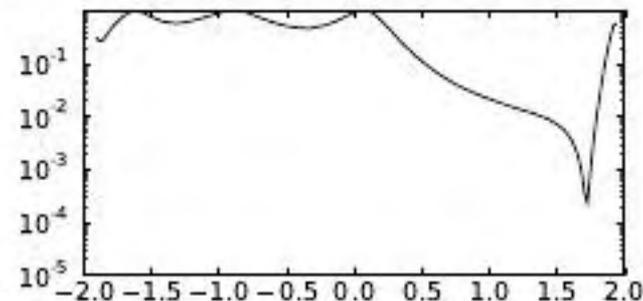
Molecule 1



Molecule 2



Molecule 3



Within a single-particle picture, the transmission probability of an electron entering a molecular junction with an energy  $E$  is given

$$T(E) = \text{Tr}[G\Gamma_L G^\dagger \Gamma_R](E) \quad (1)$$

where  $G = (E - H_{\text{mol}} - \Sigma_L - \Sigma_R)^{-1}$  is the Green function of the contacted molecule,  $\Sigma_{L/R}$  is the self-energy due to the left/right lead, and  $\Gamma_{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^\dagger)$ . Let us assume that the Hamiltonian describing the molecule is given in terms of a basis consisting of localized atomic-like orbitals,  $\phi_1, \phi_2, \dots, \phi_N$ , and that only the two orbitals  $\phi_1$  and  $\phi_N$  couple to the leads. In this case the transmission reduces to

$$T(E) = \gamma(E)^2 |G_{1N}(E)|^2. \quad (2)$$

Often the energy dependence of the lead coupling strength,  $\gamma$ , can be neglected. It then follows that the transport properties are entirely governed by the matrix element  $G_{1N}(E)$ . The latter can be obtained using Cramer's rule

$$G_{1N}(E) = \frac{C_{1N}(E - H_{\text{mol}})}{\det(E - H_{\text{mol}} - \Sigma_L - \Sigma_R)} \quad (3)$$

where  $M_{1N}(E - H_{\text{mol}})$  is the  $(1N)$  co-factor of  $E - H_{\text{mol}}$  defined as the determinant of the matrix obtained by removing the 1st row and  $N$ th column from  $E - H_{\text{mol}}$  and multiplying it by  $(-1)^{1+N}$ .

## Where is the minimum? (1)

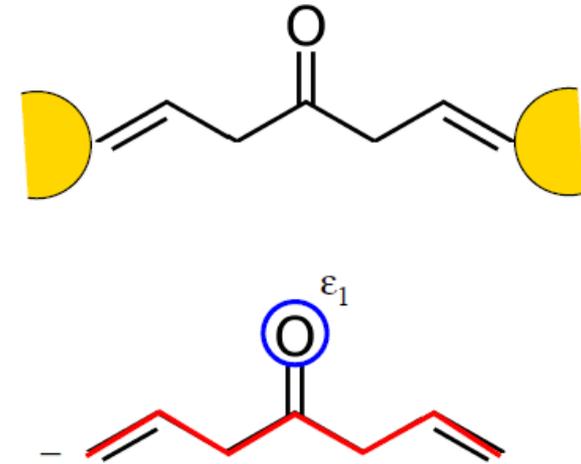
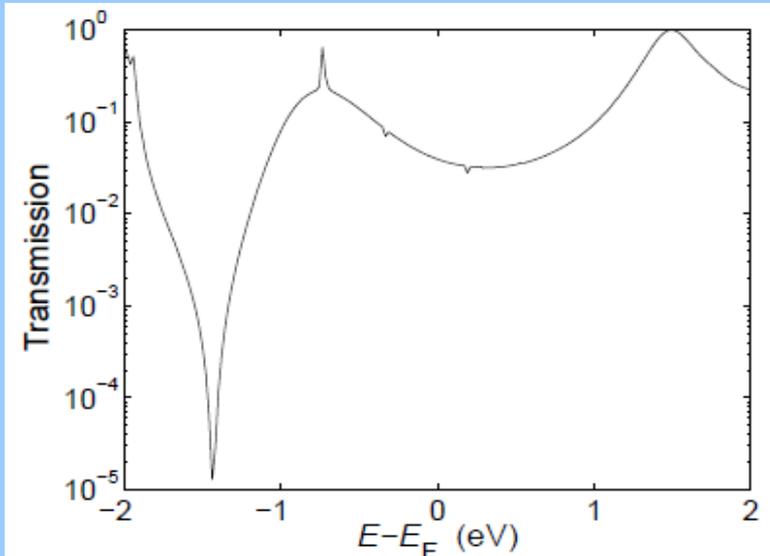
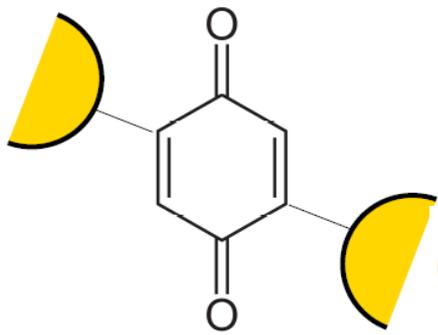


Figure 1: Junction setup for a C7 chain with an oxygen side group (top). The generalized diagram is shown in the bottom.

$$-(\varepsilon_1 - E)t^6 = 0 \Rightarrow E = \varepsilon_1.$$

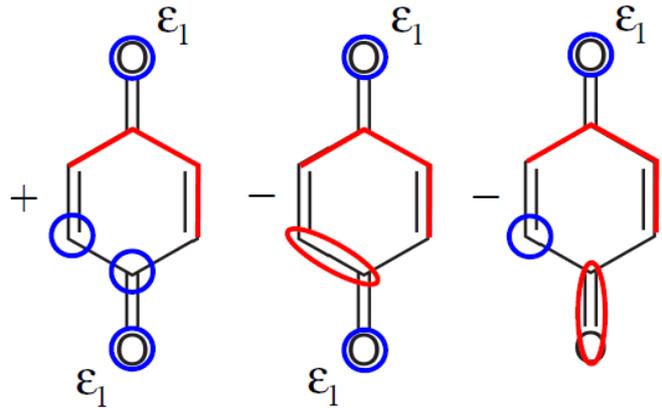


# Where is the minimum? (2)



$$(\varepsilon_1 - E)t^3 [(-E)^2(\varepsilon_1 - E) - t^2(\varepsilon_1 - E) - t^2(-E)] = 0 \quad (5)$$

T. Markussen, R. Stadler and K. Thygesen  
 Phys. Chem. Chem. Phys. **13** (2011) 14311



$$(-E)^2(\varepsilon_1 - E) - t^2(\varepsilon_1 - E) - t^2(-E) = 0$$

$$E^3 - \varepsilon_1 E^2 - 2t^2 E + t^2 \varepsilon_1 = 0. \quad (6)$$

Figure 3: Junction setup for a benzoquinone (top) and all the generalized diagrams (bottom).

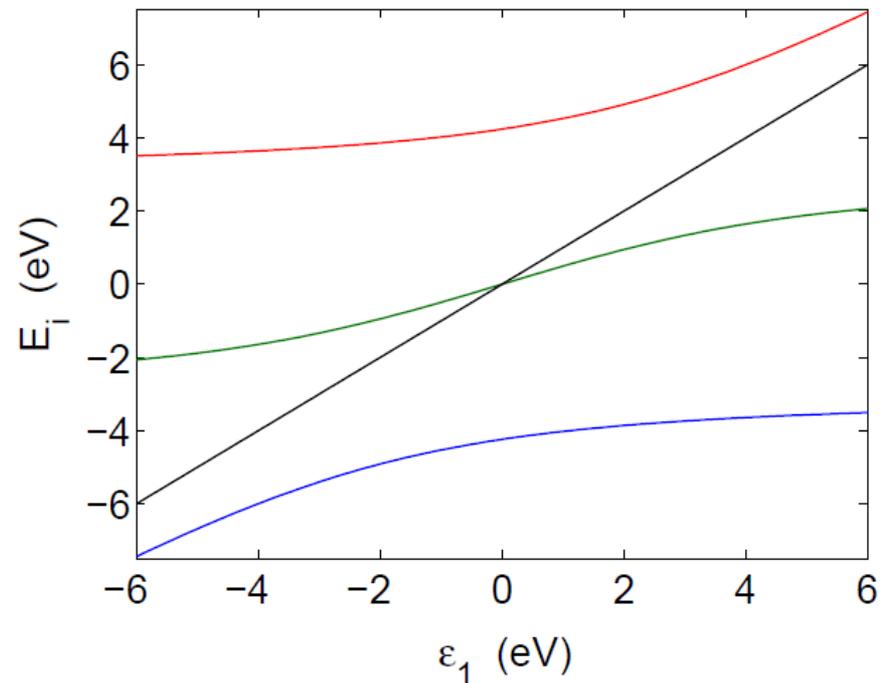
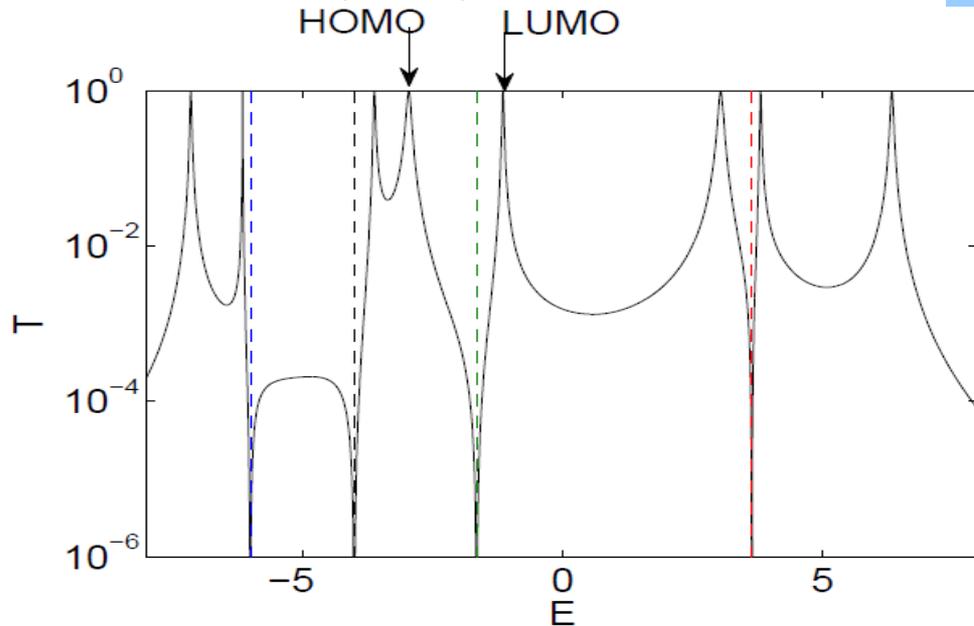


Figure 4: Transmission zeros for the benzoquinone as function of side group on-site energy,  $\varepsilon_1$ .

# Fano (1)

PHYSICAL REVIEW B **74**, 193306 (2006)

## Control of electron transport through Fano resonances in molecular wires

T. A. Papadopoulos, I. M. Grace, and C. J. Lambert

*Department of Physics, Lancaster University, Lancaster, United Kingdom*

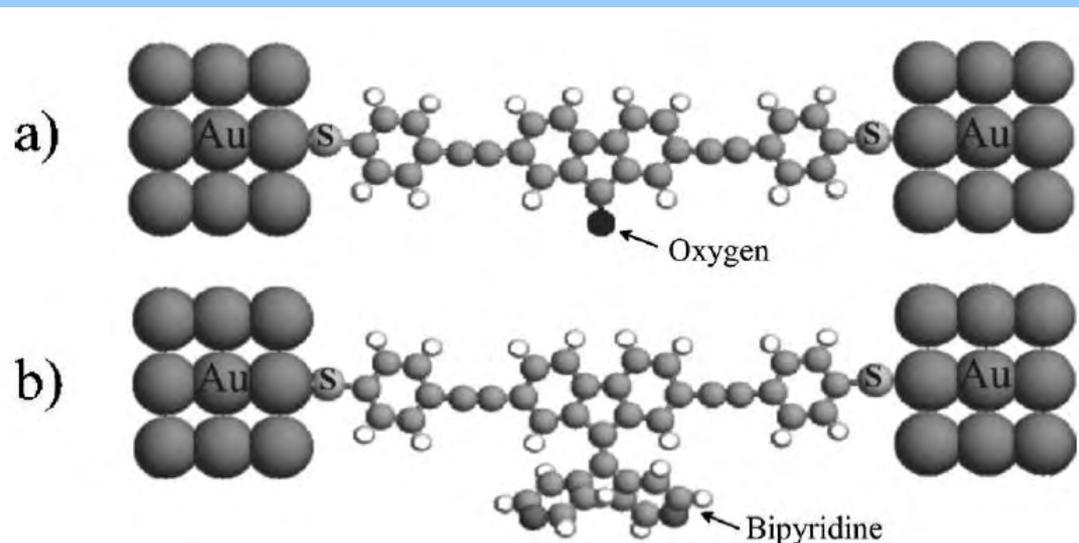


FIG. 1. The ground state geometry of the 2.5 nm molecules extended to self-consistently include eight layers of gold on the (111) surface, each containing nine Au atoms. Color codes: C (grey), H (light grey), N (dark grey), and O (black). (a) The top molecule contains a single oxygen atom attached to the central fluorene unit and (b) the oxygen has been replaced by a bipyridine unit.

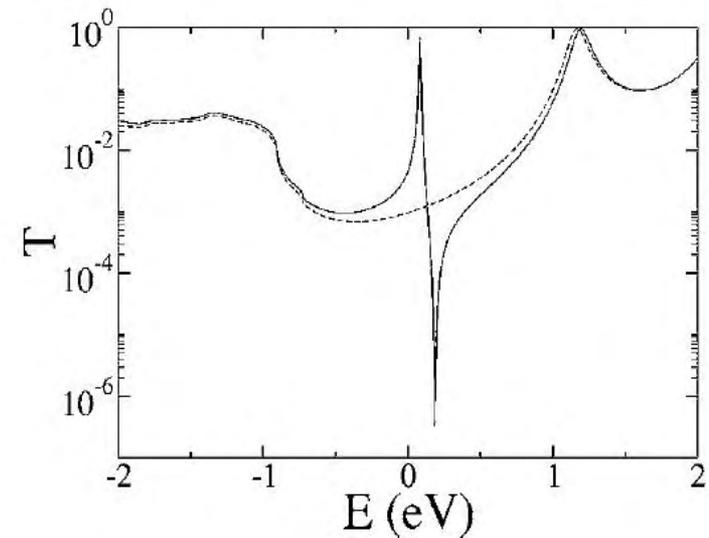


FIG. 2. Solid line: Electron transmission coefficient versus energy for the molecule having attached an oxygen atom as a side group. Dashed line: Oxygen bonds removed from the Hamiltonian.

# Fano (2)

**A**N earlier paper,<sup>1</sup> referred to here as I, pointed out that the profiles of absorption lines in the ionization continuum of atomic (and molecular) spectra are represented by the formula

$$\sigma(\epsilon) = \sigma_a [(q + \epsilon)^2 / (1 + \epsilon^2)] + \sigma_b. \quad (1.1)$$

Here

$$\epsilon = (E - E_r) / \frac{1}{2}\Gamma \quad (1.2)$$

indicates the departure of the incident photon energy  $E$  from an idealized resonance energy  $E_r$  which pertains to a discrete auto-ionizing level of the atom; this departure is expressed in a scale whose unit is the half-width  $\frac{1}{2}\Gamma$  of the line ( $\hbar/\Gamma$  is the mean life of the discrete level with respect to auto-ionization). Also,  $\sigma(\epsilon)$  represents the absorption cross section for photons of energy  $E$  whereas  $\sigma_a$  and  $\sigma_b$  represent two portions of the cross section corresponding, respectively, to transitions to states of the continuum that do and do not interact with the discrete auto-ionizing state (I, Sec. 4). Finally  $q$  is a numerical index which characterizes the line profile as shown in Fig. 1 of I. The values of  $q$ ,  $\Gamma$ ,  $\sigma_a$ , and  $\sigma_b$  are regarded as practically energy independent in the proximity of a line. The theory was applied in I only to then existing evidence<sup>2</sup> on the excitation of the  $2s2p$  level of helium by electron bombardment. Arguments were presented indicating that  $q$  should be negative for that level.

## Effects of Configuration Interaction on Intensities and Phase Shifts\*

U. FANO  
National Bureau of Standards, Washington, D. C.  
(Received July 14, 1961)

## Line Profiles in the Far-uv Absorption Spectra of the Rare Gases

U. FANO AND J. W. COOPER  
National Bureau of Standards, Washington, D. C.  
(Received 31 August 1964)

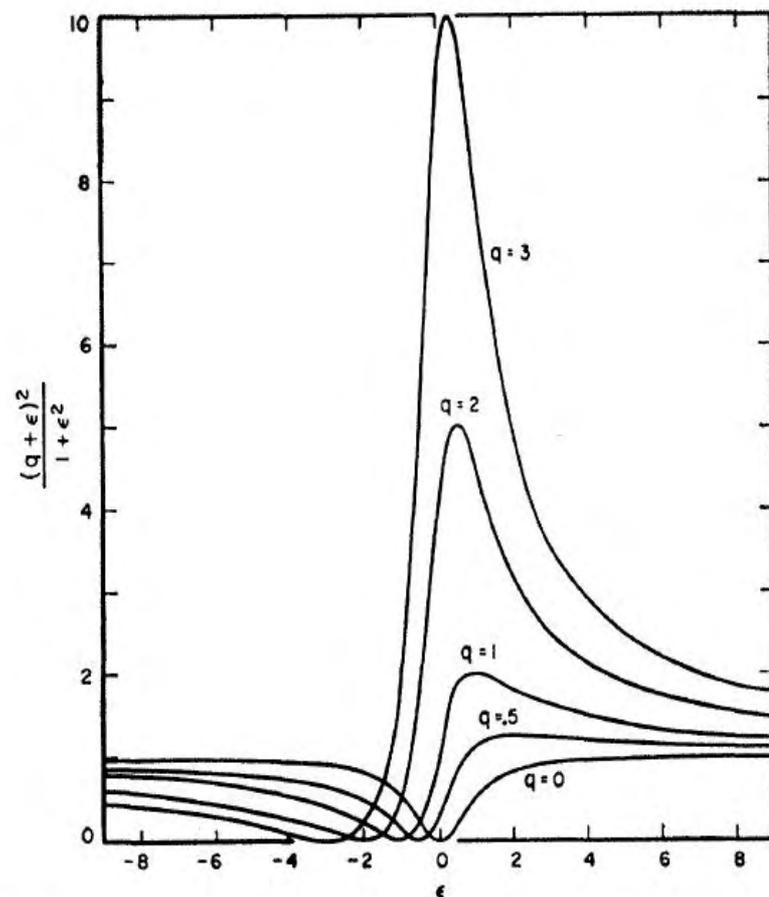


FIG. 1. Natural line shapes for different values of  $q$ . (Reverse the scale of abscissas for negative  $q$ .)

# Fano (3)

REVIEWS OF MODERN PHYSICS, VOLUME 82, JULY–SEPTEMBER 2010

## Fano resonances in nanoscale structures

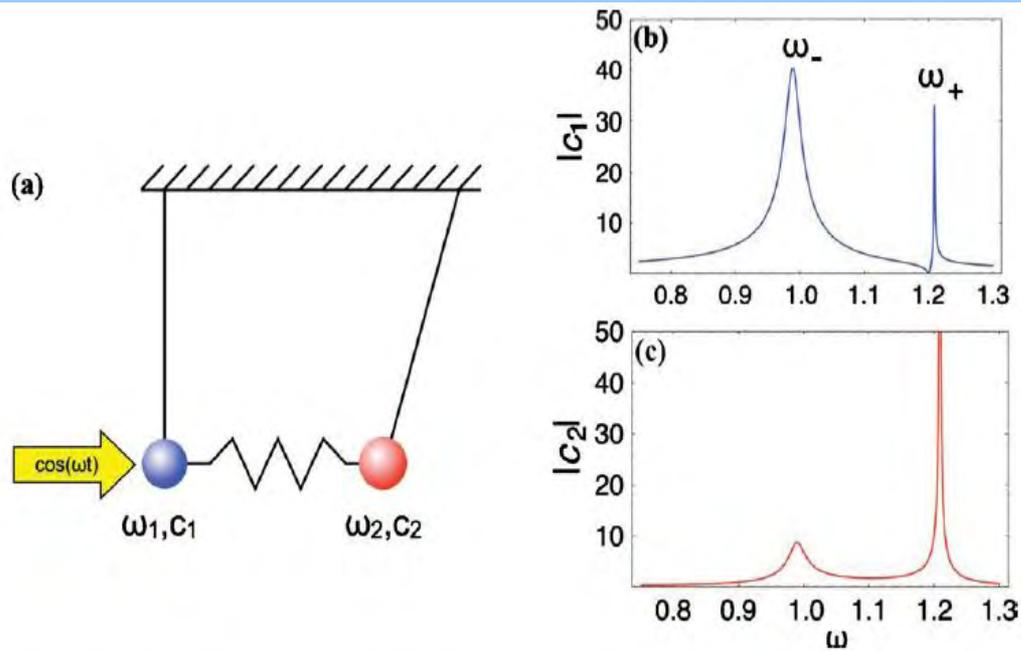


FIG. 2. (Color online) Resonances of parametrically driven coupled oscillators. (a) Schematic view of two coupled damped oscillators with a driving force applied to one of them; (b) the resonant dependence of the amplitude of the forced oscillator  $|c_1|$ , and (c) the coupled one  $|c_2|$ . There are two resonances in the system. The forced oscillator exhibits resonances with symmetric and asymmetric profiles near the eigenfrequencies  $\omega_1 = 1$  and  $\omega_2 = 1.2$  (b), respectively. The second coupled oscillator responds only with symmetric resonant profiles (c). Adapted from Joe *et al.*, 2006.

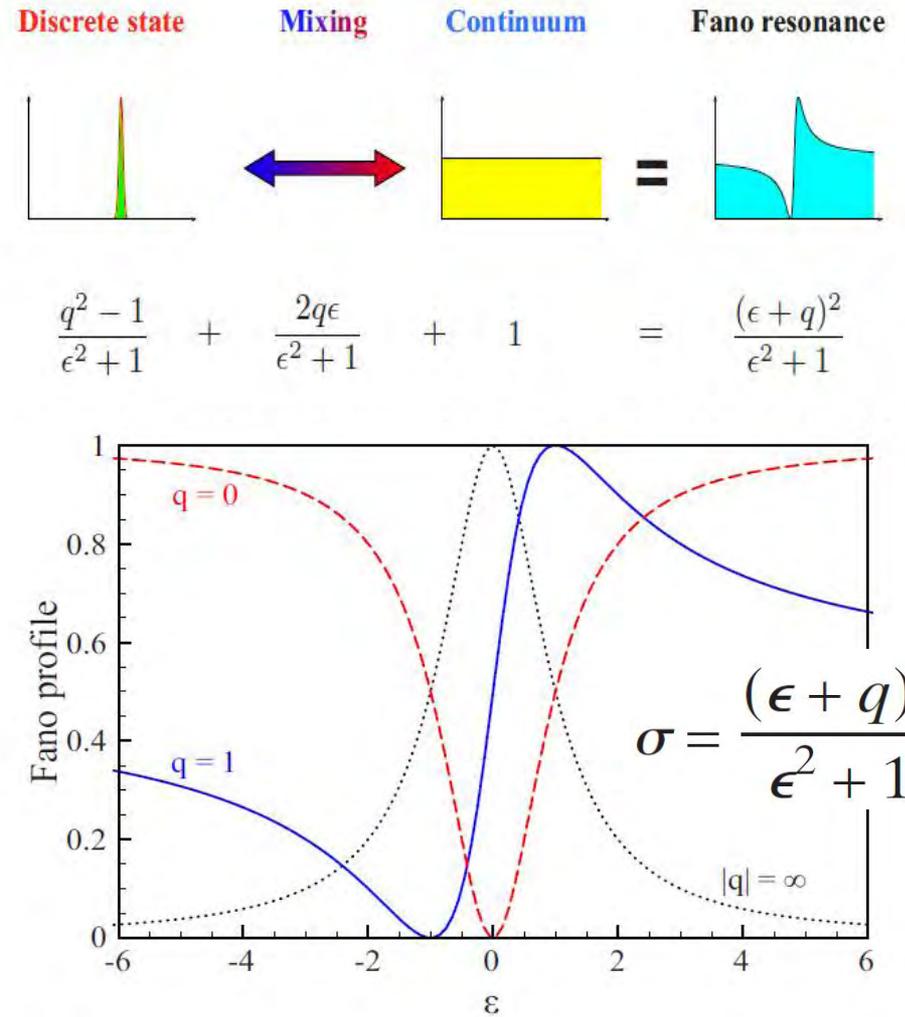


FIG. 5. (Color online) Normalized Fano profiles (1) with the prefactor  $1/(1+q^2)$  (2) for various values of the asymmetry parameter  $q$ .

## Antiresonances in molecular wires

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**J. Phys.: Condens. Matter **11** (1999) 6911–6926.**

What is particularly interesting about this molecular mechanism, and differentiates it qualitatively from a standard multi-beam interference problem encountered in optics via a diffraction grating, is that the antiresonances arise from *interference between molecular states that differ in energy*. It is also not possible to make an analogy between this effect and Fano resonances [30], which are a good analogue of the antiresonances in electron waveguides of the stub-tuner type [21]. For those waveguides, the antiresonances arise from interference between the direct transmission of a continuum of electron modes (which exists in the semiconductor quantum wire) and transmission via discrete modes that reside within the resonator. In our model, transmitted electrons *must* pass through the molecule, so there is no *direct* transmission of continuum modes from the left to the right lead and the Fano mechanism does not apply.

# Thermopower and figure of merit

PHYSICAL REVIEW B **79**, 033405 (2009)

## Giant thermopower and figure of merit in single-molecule devices

C. M. Finch,\* V. M. García-Suárez, and C. J. Lambert

The thermoelectric coefficients  $S$ ,  $G$ , and  $\kappa$  can be computed by extending the Landauer-Büttiker formalism to include both charge and heat currents. In the linear temperature and bias regime the three required thermoelectric coefficients<sup>24</sup> can be expressed in terms of the moments  $L_n$  of the transmission coefficient via the following equations,<sup>25</sup>

$$S = -\frac{1}{eT} \frac{L_1}{L_0}, \quad (2)$$

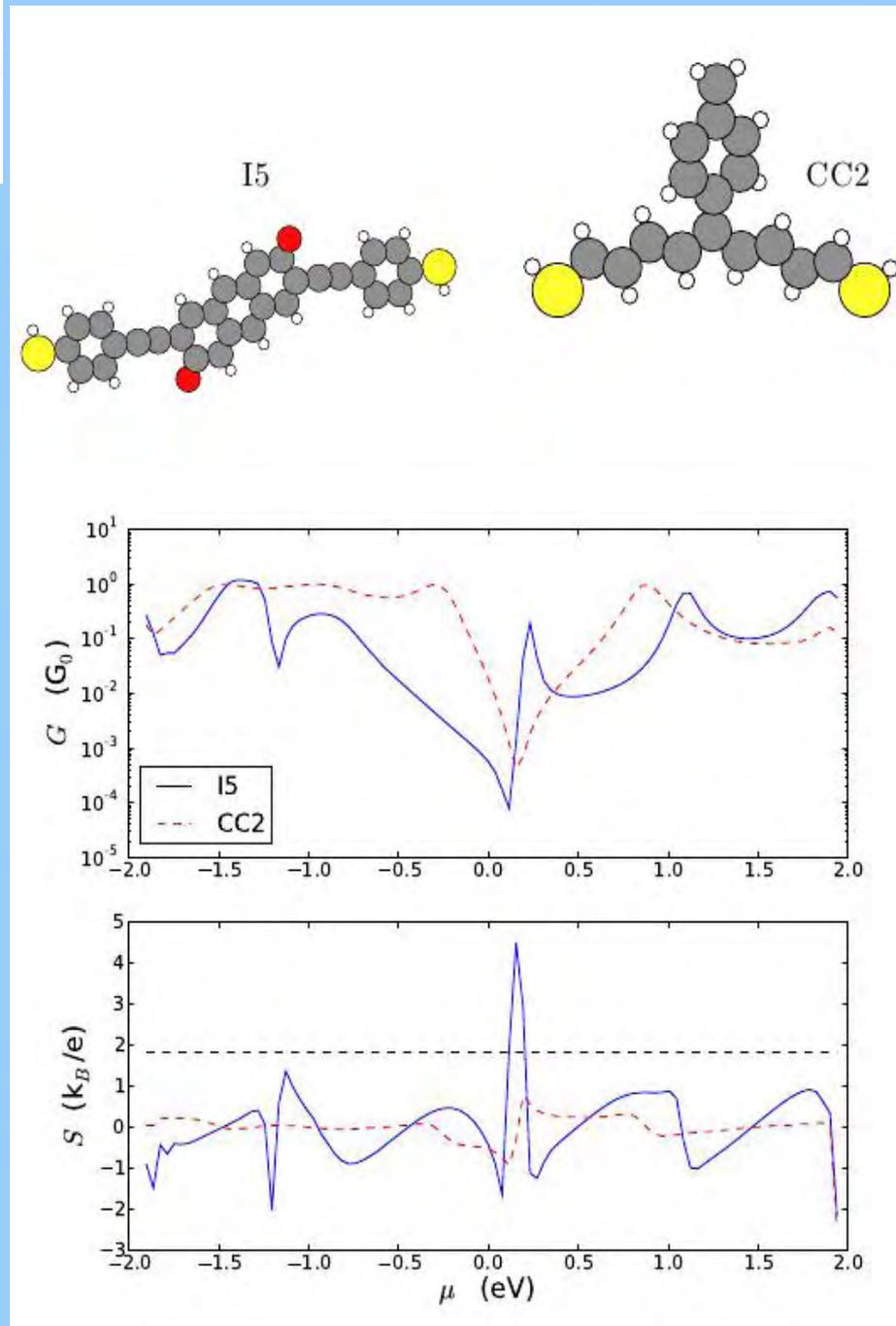
$$G = \frac{2e^2}{h} L_0, \quad (3)$$

$$\kappa = \frac{2}{hT} \left( L_2 - \frac{L_1^2}{L_0} \right), \quad (4)$$

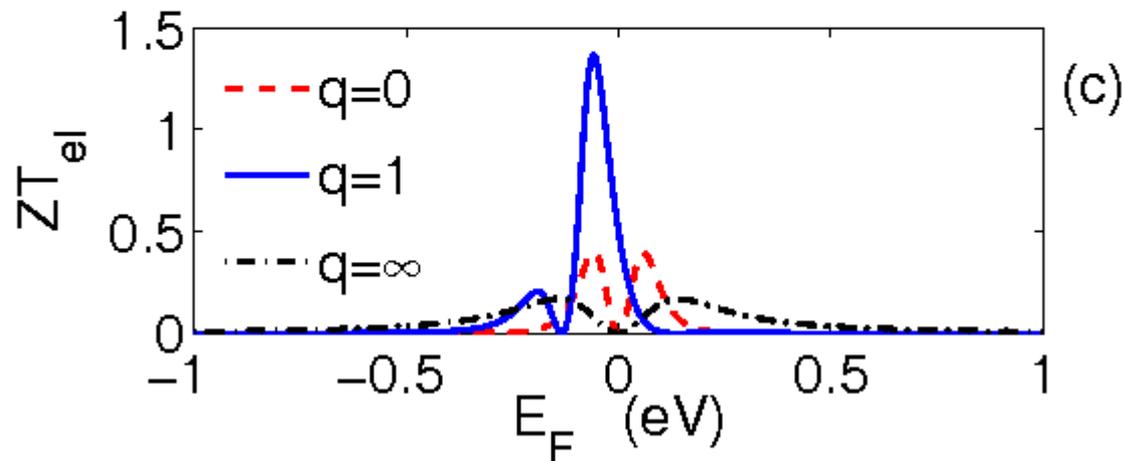
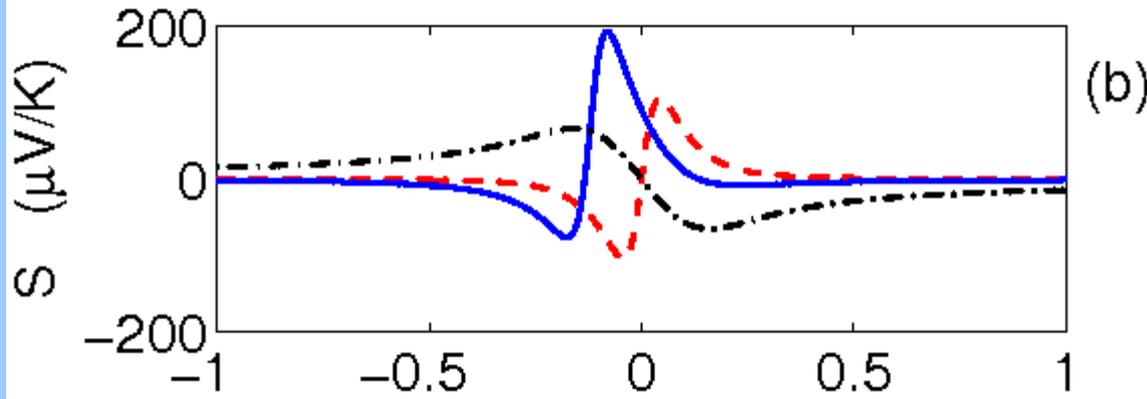
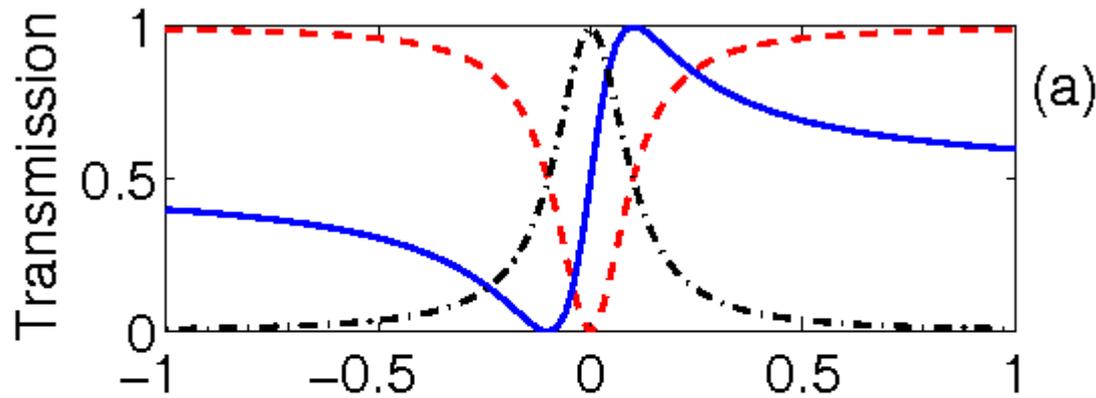
$$ZT = \frac{1}{\frac{L_0 L_2}{L_1^2} - 1}, \quad (5)$$

$$L_n = \int_{-\infty}^{\infty} (E - E_f)^n T(E) \frac{\partial f(E)}{\partial E} dE. \quad (6)$$

If  $T(E)$  is a slowly varying function of  $E$ , then at low temperatures, these expressions can be simplified by expanding  $T(E)$  about  $E = E_f$ . In the present case, where  $T(E)$  varies rapidly when a Fano resonance is present, we calculate the full integrals rather than taking the low-temperature limit.



# Explicit Fano function for the transmission



$$\mathcal{T}(E) = \frac{(q\Gamma/2 + E)^2}{(1 + q^2)(E^2 + \Gamma^2/4)}$$

$$S = \frac{T(\pi k_B)^2}{3e} \left. \frac{d \ln(\mathcal{T}(E))}{dE} \right|_{E_F}$$

$$ZT = \frac{S^2 G T}{\kappa_{el}} \cdot \frac{\kappa_{el}}{\kappa_{ph} + \kappa_{el}}$$

# Two site – tight binding model

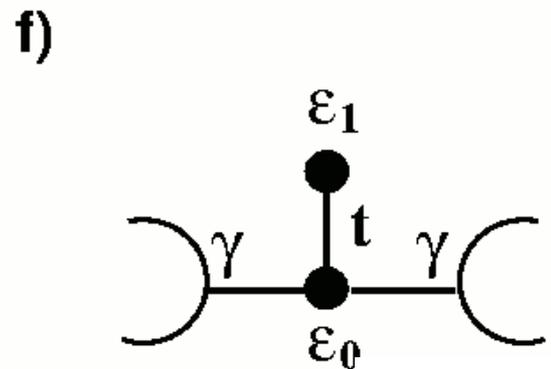
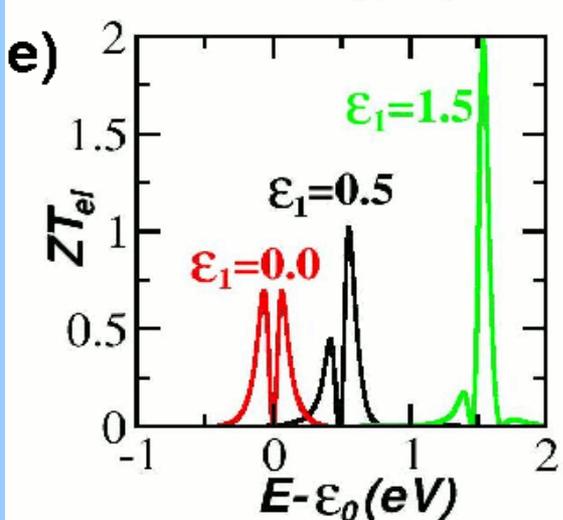
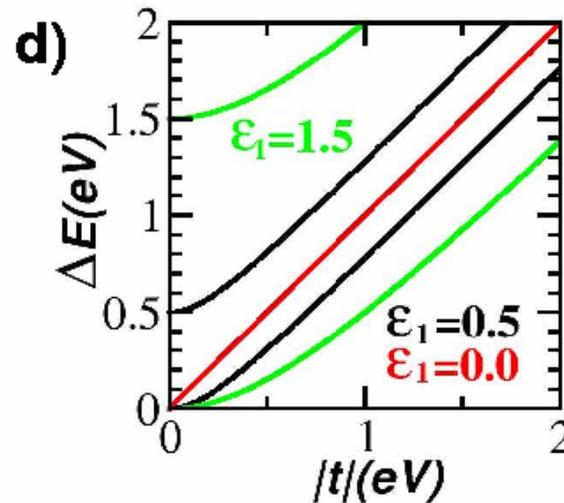
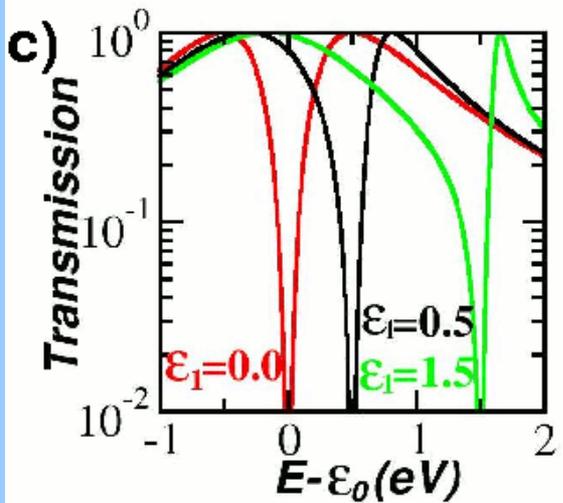
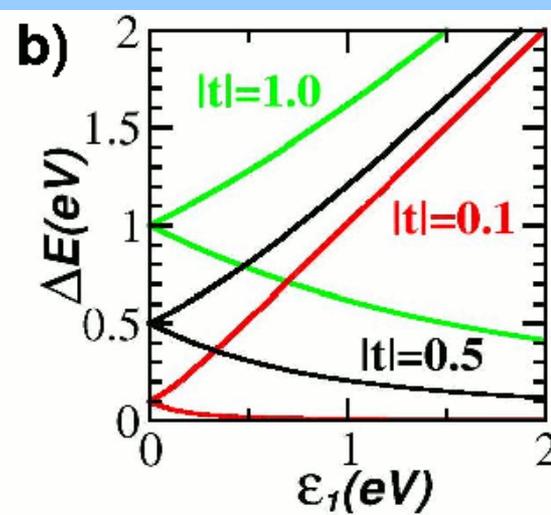
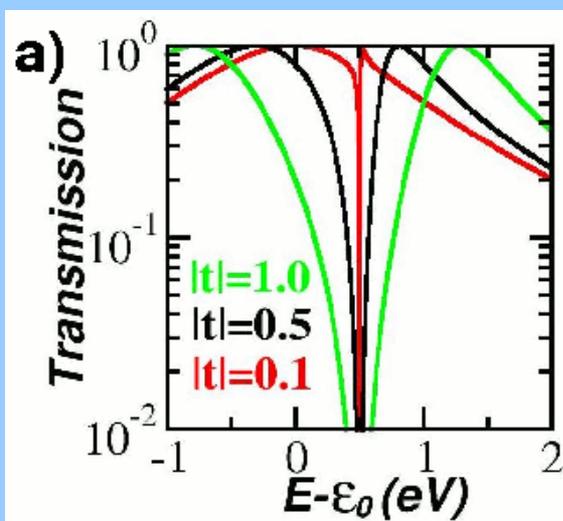
$$T(E) = \frac{4\gamma^2}{(E - \varepsilon_0 - \frac{t^2}{E - \varepsilon_1})^2 + 4\gamma^2}$$

From a simple TB model of two levels, where one is coupled to the leads and the other represents the side group analytical expressions for the minimum and two maxima in  $T(E)$  can be derived.

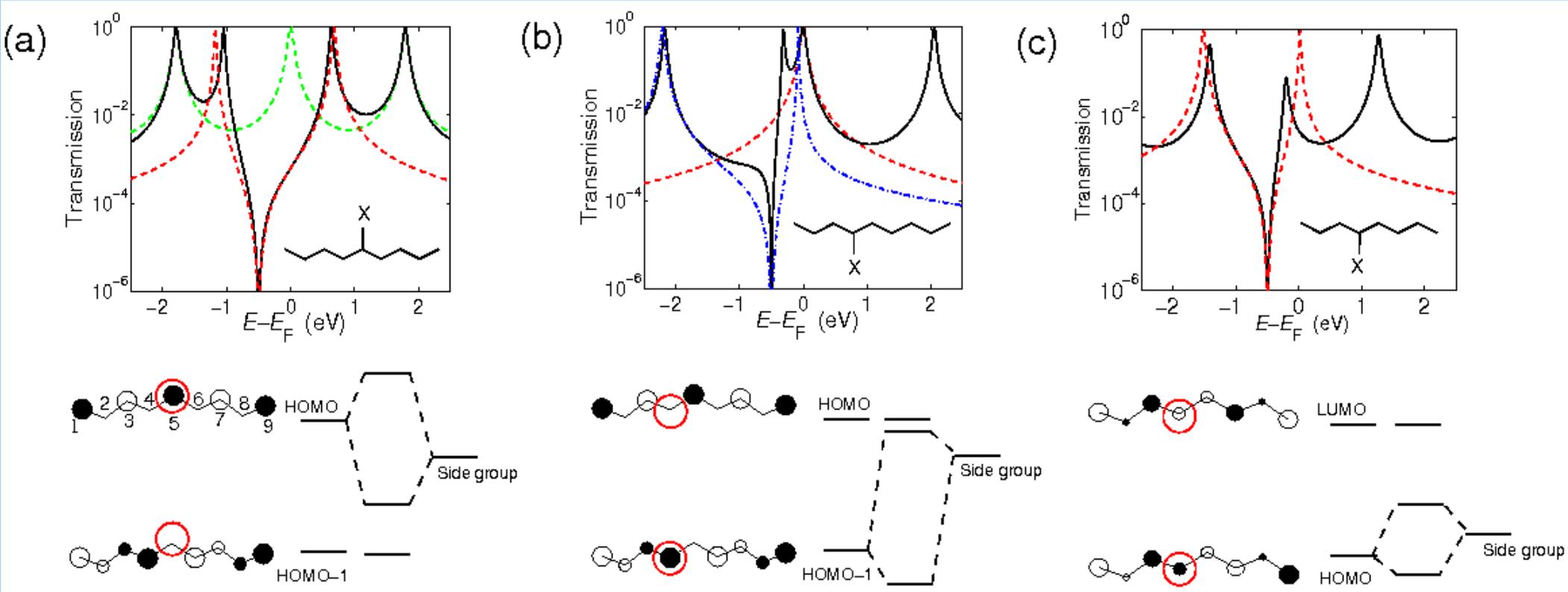
$$E_0 = \varepsilon_1$$

$$E_{1,2} = \frac{\Delta\varepsilon}{2} \pm \frac{1}{2} \sqrt{\Delta\varepsilon^2 + 4t^2}$$

$$|E_{1,2} - E_0| = \left| -\frac{\Delta\varepsilon}{2} \pm \frac{1}{2} \sqrt{\Delta\varepsilon^2 + 4t^2} \right|$$



# Molecular orbital analysis (1)



TB-AO representation of C chains with sidegroup X at -0.5 eV (CH<sub>2</sub>)

**C9-X-5**

$$\Delta\varepsilon = |0.5| \text{ eV}$$

$$t = -1.07 \text{ eV}$$

**C9-X-4**

$$\Delta\varepsilon = |1.49| \text{ eV}$$

$$t = -1.02 \text{ eV}$$

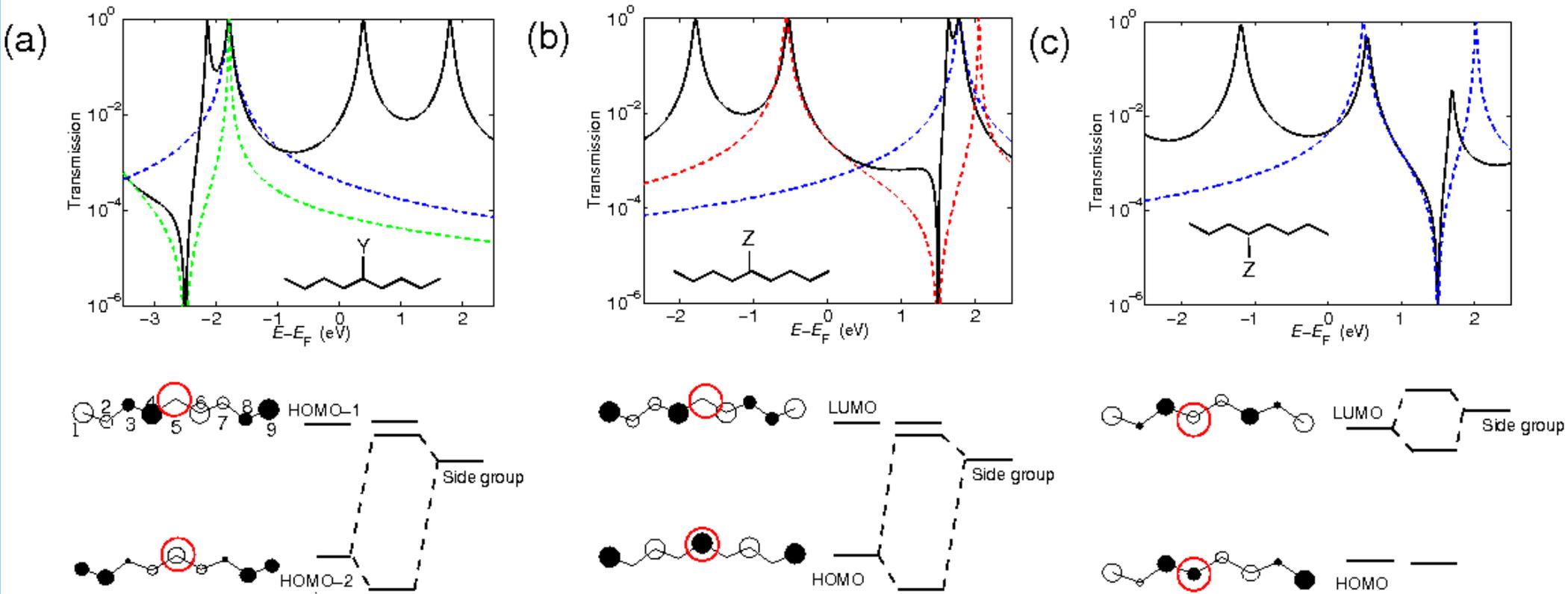
**C8-X-4**

$$\Delta\varepsilon = |0.5| \text{ eV}$$

$$t = 0.73 \text{ eV}$$

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# Molecular orbital analysis (2)



TB-AO rep. of C chains with sidegr. Y at -2.5eV (O) and 1.5eV (NO<sub>2</sub>)

**C9-Y-5**

$$\Delta\varepsilon = |0.91| \text{ eV}$$

$$t = 1.07 \text{ eV}$$

**C9-Z-5**

$$\Delta\varepsilon = |1.5| \text{ eV}$$

$$t = -1.07 \text{ eV}$$

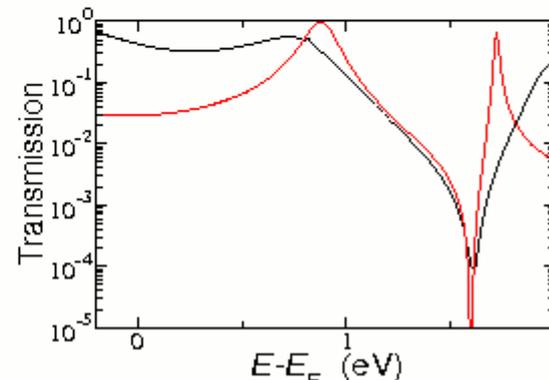
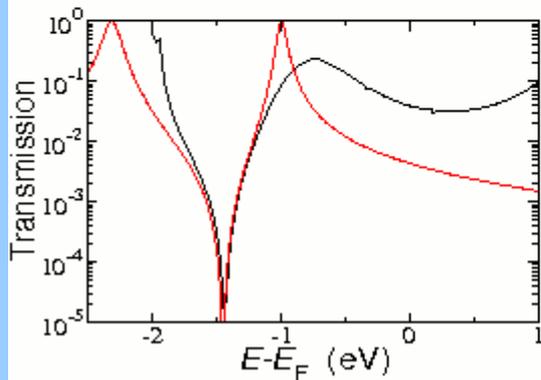
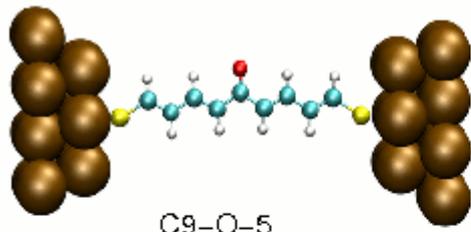
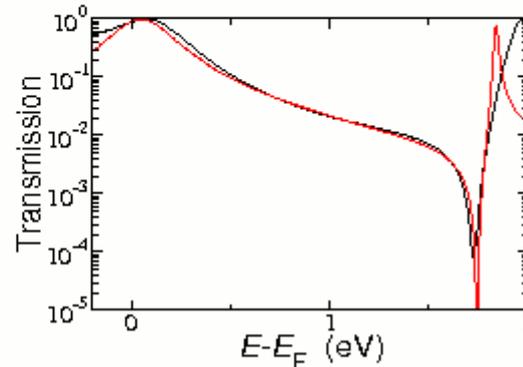
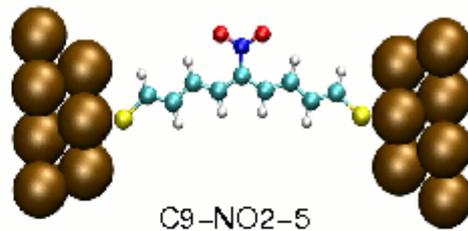
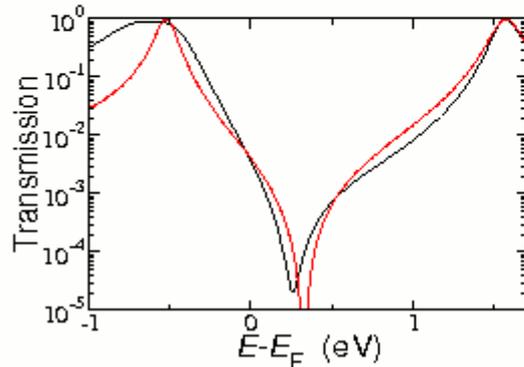
**C8-Z-4**

$$\Delta\varepsilon = |0.5| \text{ eV}$$

$$t = 0.73 \text{ eV}$$

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# DFT-results (1)



Only the topologies from the TB molecular orbital analysis corresponding to neutral molecules were investigated with density functional theory based electron transport calculations, and not those corresponding to radicals or diradicals.

In all studied systems the peak shapes obtained from DFT are very close to those from TB calculations, which confirms that they are indeed completely defined by the topologies of  $p_z$  orbitals.

## DFT-results (2)

Molecule	C9-CH <sub>2</sub> -5	C9-O-4	C8-NO <sub>2</sub> -4	C9-NO <sub>2</sub> -5
$ \Delta\varepsilon $	0.40	0.91	0.61	1.60
$ t_{sg} $	1.03	1.12	0.32	0.40
$E_0$	0.26	-1.44	1.61	1.72
$ \Delta E $	0.89	0.65	0.40	0.20
$S(E)$	-170 (0.21)	184 (-1.39)	199 (1.65)	349 (1.74)
$ZT_{el}(E)$	0.82 (0.19)	0.93 (-1.37)	1.00 (1.67)	3.00 (1.77)
$ZT(E)$	0.003 (0.19)	0.01 (-1.37)	0.03 (1.67)	0.48 (1.77)

Also the DFT results show the same dependency on  $\Delta\varepsilon$  and  $t$  as the TB models, which is sufficient to explain the trends in  $ZT_{el}$  and even in  $ZT$ , where a constant value of the thermal conductance (50 pW/K) has been assumed to account for the phonon contributions.

**R. Stadler and T. Markussen, J. Chem. Phys. 135 (2011) 154109**

# Conclusions

- 1) **Quantum interference effects (QIE)** can induce dips in the transmission function, thereby reducing the conductance by several orders of magnitude, for conjugated organic molecules with side groups. The dependency of the occurrence of QIE on the **molecular structure (configuration)** can be already studied and understood on the level of topological tight binding models, where **simple graphical rules** can be derived.
- 2) The **structure dependence of the peak shape** of such QI induced dips is highly relevant for some applications such as **thermoelectric devices** and there is some resemblance with so-called **Fano peaks**.
- 3) I presented a study of the dependence of the peak shape on two parameters in **2-site tight-binding models** with the aim of **mapping the structural properties of molecular wires with sidegroups** onto this models. This should provide a route towards investigating the **structure dependence of the peak shapes** systematically, and enable the **chemical engineering** of this property.

**Thank you for your attention!**